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THEORETICAL AND EXPERIMENTAL YIELDS OF STYRENE IN THE CATALYTIC DEHYDROGENATION OF ETHYLBENZENE

N. I. Shuikin and I. I. Levitsky

Calculations of the equilibrium constants for the dehydration of ethylbenzene were first published in the literature in 1943 by Guttman, Westrum and Pitzer [1]. These authors point out (without giving numerical data) that their calculated equilibrium values for the extent of dehydrogenation within the range 425-500° are close to the experimental values obtained by Sergienko [2]. At higher temperatures the calculated values are greater than the experimental, which Guttman and his co-workers attribute to the development of side reactions.

However, similar discrepancies between the theoretical and experimental yields of styrene have been utilized in some papers to support the assumption that the dehydrogenation of ethylbenzene does not reach an equilibrium state (or reversibility), and that the yields of styrene are determined only by the reaction velocity. Marukyan studied the dehydrogenation of several alkylbenzenes and established [3] some relationships concerning the connection between the structure of the alkylbenzenes and their relative dehydrogenation rates. This assumption served as a basis for the creation of a new fragment of the multiplet theory, "the quintet mechanism of dehydrogenation" [4], according to which the dehydrogenation of ethylbenzene and the diethylbenzenes takes place at the active center of five atoms ("quintet") when the molecules are densely oriented on the catalyst surface. The basis for the presentation of these concepts was the assumption that the yields of styrene were determined solely by the velocity of dehydrogenation of ethylbenzene. This assumption was prompted by the fact that the thermodynamic calculation provided evidence that equilibrium was not established [3].

Wenner and Dybdal [5] also associated the discrepancies between the theoretical and experimental yields of styrene with the absence of equilibrium. These authors calculated the velocity constant for the dehydrogenation of ethylbenzene from the following equation:

$$\frac{dS}{dW} = k\left(P_{eb.} - \frac{P_{st.}\,P_H}{K_E}\right)$$

where dS is the amount of styrene produced in 1 hour in a volume element containing dW of catalyst; k is the velocity constant; K_E is the equilibrium constant; $P_{eb.}$, $P_{st.}$ and P_H are the partial pressures of ethyl benzene, styrene and hydrogen in the reaction zone. We shall return to the results of this work later.

In recent years many authors [6,7,8,9] have published data for thermodynamic calculations on the dehydrogenation of ethylbenzene. All these data have been obtained by the method of statistical thermodynamics, and they lead to almost identical equilibrium constants. The work of Ghosh [10] and his co-workers is the only experimental study on the thermodynamic equilibrium of the reaction. In this work the dehydrogenation of ethyl-

benzene was studied at low pressures (11 to 40 mm Hg) within the temperature range 360 to 495°. The equilibrium constants determined by these authors are greater than those which we have calculated from the data of Vvedensky, Korobov and Frost, Kilpatrick, Rossini and others [6,7,8]. Thus, for example, Ghosh and his co-workers obtained a value of $K_E = 0.031$ at 495°, but our calculated value for the same temperature is $K_E = 0.024$. The difference in the yields of styrene calculated from these values of K_E amounts to only 2% (the corresponding yields are 17.3 and 15.5%).

In our investigation of the mode of action of inert diluents on the catalytic dehydrogenation of ethylbenzene it was established that this reaction reaches a state of thermodynamic equilibrium over a wide range of molar velocities [11]. All the thermodynamic calculations in this investigation were based on equilibrium constants obtained from experimental data, due allowance being made for side reactions (polymerization, cracking). In this work it was also noted that the styrene content of the catalyzation product (obtained at 575°) was 9% less than the theoretical yield.

In the present paper a systematic comparison is made between the theoretical yields of styrene from ethylbenzene and experimental values obtained under the conditions which are ordinarily used for the reaction. These conditions did not exclude the possible development of side reactions, and for this reason the data cannot be used as a basis for checking the equilibrium constants. It should be mentioned that in the literature not only is such a comparison not described, but even values for the theoretical yields of styrene from ethylbenzene are lacking. The calculation of these values is therefore given below.

Calculation of the Thermodynamic Equilibrium for the Dehydrogenation of Ethylbenzene

The equilibrium constants for the dehydrogenation of ethylbenzene were calculated from the equation [12]:

$$R \cdot \ln K_E = -\left(\Delta \frac{F^0 - H_0^0}{T} + \frac{\Delta H_0^0}{T}\right).$$

Here R is the gas constant; $\Delta \frac{F^0 - H_0^0}{T}$ is the difference between the corresponding functions for the reaction products (styrene and hydrogen) and the starting-material (ethylbenzene); ΔH_0^0 is the heat of dehydrogenation of ethylbenzene (cal/mole at 0°K); T is the temperature in degrees K.

Values of the function $\left(\frac{F^0 - H_0^0}{T}\right)$ for hydrogen, styrene, and ethylbenzene were taken from the monograph of Vvedensky [6]. The heat of dehydrogenation of ethylbenzene at zero absolute (ΔH_0^0) was calculated from the heats of formation of ethylbenzene and styrene at the same temperature. The heat of formation of the hydrocarbons (styrene and ethylbenzene) at 0°K was calculated as the difference between the heat of formation at 298°K and the corresponding change in enthalpy $\Delta(H_{298}^0 - H_0^0)$. The enthalpy values of hydrogen, graphite, ethylbenzene and styrene at 298°K and the heat of formation of ethylbenzene at the same temperature were taken from Vvedensky's monograph [6]. The value for the heat of formation of styrene at 298°K was derived from the data of Prosena and Rossini [13].

The heats of formation at 0°K calculated in this way were found to be: 13,917 cal/mole for ethylbenzene and 40,340 cal/mole for styrene. The heat of dehydrogenation of ethylbenzene at 0°K is therefore 26,423 cal/mole.

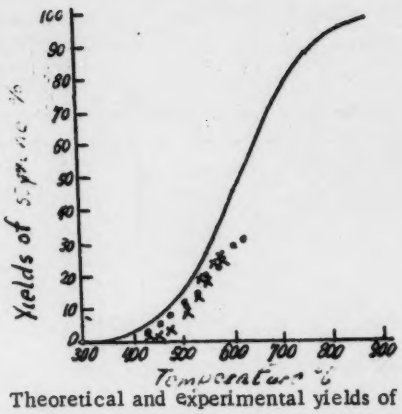
The method we used for calculating the equilibrium constants is of interest, because the heats of formation of the hydrocarbons are the only thermodynamic quantities on which the calculations are based; all the other data needed were obtained by the methods of statistical thermodynamics.

The calculation of the equilibrium yields of styrene from values of K_E was described in our previous paper [11]. Values of K_E for the dehydrogenation of ethylbenzene, calculated in the manner described, and values for the degree of completeness of the reaction at equilibrium are shown in Table 1 and also on the graph.

TABLE 1

Equilibrium Constants and Values for the Degree of Completeness of the Dehydrogenation of Ethylbenzene

Temperature °C	Equilibrium constant(K_E)	Degree of completeness of dehydrogenation of ethylbenzene,%
127	$5.058 \cdot 10^{-10}$	$2.25 \cdot 10^{-3}$
227	$7.178 \cdot 10^{-7}$	$8.47 \cdot 10^{-2}$
327	$9.683 \cdot 10^{-5}$	0.98
427	$3.296 \cdot 10^{-3}$	5.74
527	$4.732 \cdot 10^{-2}$	21.78
627	$3.784 \cdot 10^{-1}$	52.39
727	2.014	81.74
827	7.870	94.20
927	24.43	98.00



Theoretical and experimental yields of styrene in the dehydrogenation of ethylbenzene — calculated; o – o experimental with $Cr_2O_3-MoO_2-Al_2O_3$; x–x experimental with $V_2O_5-Al_2O_3$.

EXPERIMENTAL

We carried out a study of the dehydrogenation of undiluted ethylbenzene at different temperatures by the method previously described [11]. Two catalysts were studied. Samples of catalyst (up to 50 mm) were not changed in the course of each whole series of experiments, and after each experiment the catalyst was regenerated by means of a stream of air (2 hours at 600°). The results of the experiments with the aluminum-chromium-molybdenum catalyst are shown in Table 2. Column 7 of this table gives values for the theoretical yield of styrene, calculated by the graphical method from the data of Table 1. The discrepancies between the theoretical and experimental yields of styrene are given in column 8. These discrepancies increase from 1.9% at 424° to 21.6% at 627°. The ethylbenzene losses show a corresponding increase from 3.7 to 14.9%. In all the experiments carried out at 424-575° the descrepancy is close to the loss, differing by only 2-3%. This agreement between these values is probably explained by the fact that the discrepancies and the losses are due to the same cause – polymerization of the styrene produced. The deposition of "tar" was always observed in that part of the catalyzation tube where the product condensed.* At higher temperatures (600-627°) values for the discrepancy are 7% higher than the loss values, which is evidently due to the partial dealkylation of the ethylbenzene starting-material.

The results of experiments carried out with an aluminum-vanadium catalyst are given in Table 3. Up to 475° this catalyst showed a very low activity. However, the styrene yields obtained within the range 525-575° were found to be very close to the corresponding yields obtained with the aluminum-chromium-molybdenum catalyst. The discrepancy and loss values (columns 8 and 9, Table 3) were also close to those described earlier.

The results obtained with these two catalysts are compared with the corresponding theoretical figures on the graph.

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* At its condensation temperature the polymerization velocity of styrene is fairly large, for example, at 150° styrene polymerizes to the extent of 80% in 5 hours. On the other hand, it would be expected that polymerization in the reaction zone would be impossible; at 350-400° polystyrene is completely depolymerized [14].

TABLE 2

Dehydrogenation of Ethylbenzene in the Presence of an Aluminum-Chromium-Molybdenum Catalyst

Expt. No.	Temperature °C	Volume velocity	Styrene content of catalyzation product, %	Yield of catalyzation product, on ethylbenzene passed, %	Yield of styrene, on ethylbenzene passed, %	Theoretical yield of styrene, %	Discrepancy, %	Loss of ethylbenzene, %
1	2	3	4	5	6	7	8	9
45	424	0.44	3.8	96.3	3.7	5.6	1.9	3.7
46	452	0.44	5.8	96.6	5.6	8.5	2.9	3.4
44	475	0.36	8.8	94.9	8.4	12.0	3.6	5.1
42	503	0.35	11.9	94.6	11.3	16.8	5.5	5.4
43	503	0.97	11.3	97.0	11.0	16.8	5.8	3.0
47	526	0.43	15.1	95.4	14.4	21.7	7.3	4.6
48	551	0.39	20.9	94.6	19.8	27.2	7.4	5.4
49	575	0.41	24.7	92.0	22.7	34.3	11.6	8.0
50	602	0.40	30.8	92.7	28.6	43.0	14.4	7.3
51	627	0.40	36.2	85.1	30.8	52.4	21.6	14.9

TABLE 3

Dehydrogenation of Ethylbenzene in the Presence of an Aluminum-Vanadium Catalyst

Expt. No.	Temperature °C	Volume velocity	Styrene content of catalyzation product, %	Yield of catalyzation product, on ethylbenzene passed, %	Yield of styrene, on ethylbenzene passed, %	Theoretical yield of styrene, %	Discrepancy, %	Loss of ethylbenzene, %
1	2	3	4	5	6	7	8	9
85	452	0.29	1.5	99.0	1.5	8.5	7.0	1.0
86	475	0.30	3.4	99.0	3.4	12.0	8.6	1.0
91	503	0.31	9.1	98.0	8.9	16.8	7.9	2.0
92	525	0.29	14.7	94.9	14.0	21.7	7.7	5.1
89	551	0.86	17.8	94.5	16.8	27.2	10.4	5.5
103	547	0.24	20.7	87.4	18.1	26.2	8.1	12.6
90	575	1.09	23.9	93.2	22.3	34.3	12.0	6.8
104*	575	1.04	24.8	94.3	23.4	34.3	10.9	5.7
107*	575	1.47	26.3	94.6	24.9	34.3	9.4	5.4
106*	575	1.91	25.4	97.2	24.7	34.3	9.6	2.8
135*	575	2.40	24.7	94.0	23.2	34.3	11.1	6.0

* An earlier [11] calculation of K_E was based on these results.

The results we have obtained are in good agreement with those of Wenner and Dybdal [5]. These authors studied the dehydrogenation of undiluted ethylbenzene in a pilot plant (catalyst volume 350 ml). In Table 4 we give (recalculating for conformity) the results obtained in this work for the temperature range 550-600°. A noteworthy feature is the lack of dependence of the styrene yields on the volume velocity for two to three-fold changes in the latter (compare experiments 232,229, 227); at the same time the styrene yields are very close to those we

TABLE 4

Dehydrogenation of Ethylbenzene in a Pilot Plant: Data of Wenner and Dybdal.

Expt. No.	Temperature °C	Volume velocity	Styrene content of catalyzation product, %	Yield of catalyzation product, on ethylbenzene passed, %	Yield of styrene, on ethylbenzene passed, %	Theoretical yield of styrene, %	Discrepancy, %	Loss of ethylbenzene, %
1	2	3	4	5	6	7	8	9
228	552	3.29	22.8	88.0	20.1	27.5	7.4	12.0
232	555	1.10	20.9	90.8	19.0	28.3	9.3	9.2
229	555	2.24	23.0	93.2	21.4	28.3	6.9	6.8
227	555	3.47	22.9	96.5	22.2	28.3	6.2	7.5
230	556	2.07	23.0	94.5	21.7	28.3	6.6	5.5
242	598	1.02	26.6	89.1	23.7	42.0	18.3	10.9
239	600	2.03	27.5	90.0	24.7	42.5	17.8	10.0
237	598	3.87	25.2	93.5	23.6	42.0	18.4	6.5

obtained (see experiment 103 and the following ones in Table 3); the equilibrium character of these was established in our previous work [11]. On the other hand, the discrepancies between the theoretical and experimental yields are close to the values for the ethylbenzene losses, which also is in full agreement with our results (compare columns 8 and 9 in Table 4 with the corresponding columns in Table 2). These losses cannot be explained by pyrolysis; in these experiments the authors observed only 0.4-0.8% of benzene and 0.6-1.7% of toluene in the catalyzation product.

It is evident that the authors of this paper were dealing with equilibrium yields of styrene. The equilibrium constants for the dehydrogenation of ethylbenzene calculated from these styrene yields are therefore somewhat doubtful. The results given here, together with those previously given [11], make it possible to assume that the discrepancies between the theoretical and experimental styrene yields are due to the development of side reactions (polymerization, dealkylation). These discrepancies can hardly be cited as proof of the assertion that the dehydrogenation of ethylbenzene does not attain a state of equilibrium; the reaction can attain a state of equilibrium, but side reactions make it impossible to obtain a theoretical yield of styrene.

SUMMARY

1. The extent of dehydrogenation of ethylbenzene at equilibrium has been calculated from thermodynamic data given in the literature. It is shown that the theoretical yields of styrene increase from 5.7% at 427° to 52.4% at 627°.

2. The dehydrogenation of ethylbenzene was investigated at different temperatures. It is shown that in the presence of an aluminum-chromium-molybdenum catalyst the yields of styrene increase from 3.7% at 424° to 30.8% at 627°, but over the same range the discrepancy between the theoretical and experimental yields increases from 1.9 to 21.6%. The activity of the aluminum-vanadium catalyst is low below 525°, but the results obtained at 525-575° are almost identical with those obtained in the corresponding experiments with the aluminum-chromium-molybdenum catalyst.

3. It is shown that values for the discrepancy between the theoretical and experimental yields of styrene are close to the values for the loss of catalyzation product. It is suggested that these discrepancies are caused by side reactions, and they cannot be taken as evidence of failure to reach equilibrium.

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* See Consultants Bureau Translation, p. 559.

THE EFFECT OF SECONDARY CONSTITUENTS ON THE NATURE OF THE SURFACE HETEROGENEITY OF SOLID BODIES AS SHOWN BY THEIR ADSORPTIVE PROPERTIES

N. M. Manko and V. I. Levin

The adsorptive and catalytic properties of solid bodies are noteworthy because of their extraordinary diversity and specificity. The activity of a solid body in a given process is essentially determined by its nature. In addition, the activity of a definite solid body in relation to one and the same substance varies within very wide limits depending on its present state and on those states through which it has passed in its formation--on its "biography."

Questions dealing with the formation of active surfaces which are closely related to the problem of preparing catalysts having suitable properties, have naturally been the subject of numerous experimental and theoretical studies. In this field, Roginsky has put forward a number of fundamental principles which may be summarized as follows:

1. An active solid body is usually in a state removed from thermodynamic equilibrium. Catalytic activity is connected with the body's excess of free energy over the value of the free energy of the same body in its normal, i.e. thermodynamically stable, state. All those conditions which increase the free energy of the catalyst or adsorbent during its preparation must also increase its activity. These hypotheses form what has been termed the supersaturation theory[1-4], and they have been confirmed in a series of experimental investigations[4-7]; they have also been successfully used in the solution of applied problems[8,9].

2. Active bodies which have been prepared in a highly supersaturated state will have structures deviating from normal, and the higher the activity, the larger will be the deviation. These structure deviations or aberrations may include all kinds of purely mechanical defects (lattice voids, structure deformations, etc.). On the other hand, chemical deviations may occur; these include local aberrations in stoichiometric composition and the intrusion of extraneous substances. From the point of view of catalysis and adsorption, the most stable, and therefore the most important, aberrations are those of a chemical nature [1].

The concept of a relationship between the catlytic activity of a solid body and its secondary constituents is confirmed by all our experience of applied catalysis. This relationship has been studied experimentally in a number of investigations, which have resulted in the establishment of certain laws governing the dependence of activity on the presence of secondary constituents. Experiments have shown that the same secondary constituent can act both as a promoter and as a poison, depending on its concentration. Moreover, a change in the proportion of secondary constituent may result in a change both in the activation energy of the process and in the pre-exponential multiplier of the velocity constant (observed). The group of phenomena associated with the action of secondary constituents on the activity of solid bodies has been termed "modification" [6, 10, 11, 12].

3. The surface of an actual solid body is heterogeneous insofar as its adsorptive and catalytic properties are concerned. This heterogeneity has a profound influence on the character of the laws governing processes which take place at its surface. For the theoretical analysis of heterogeneous-surface processes, a statistical method is used, which has been most fully developed by Roginsky[10,13]. Fundamental to this method is the concept of a distribution function of values of some parameter over area-elements of the surface. This distribution function is a surface characteristic of a given solid body, considered in relation to some definite process.

Most of the experimental applications of the statistical method have been made in the study of activated adsorption [9, 13, 14, 15, 18]. In this case, the surface characteristic used in the distribution function is the adsorption activation energy. The relation between the type of distribution function and the character of the kinetic adsorption equations corresponding to the function, as well as the methods used for deriving distribution functions from experimental data, have already been discussed in sufficient detail [10, 13, 14, 15, 16, 17].

If we start from the idea of a relationship between the activity of a solid body and its content of secondary constituents it is natural to attribute the surface heterogeneity, as shown by its catalytic and adsorptive properties, to the action of these constituents. The formation of some kind of distribution of active centers, according to their degree of activity, must be connected with the presence of secondary constituents of a definite nature and in a definite concentration.

For this reason, experimental and theoretical studies on the effect of admixtures on the character of the surface heterogeneity of adsorbents and catalysts are of undoubted interest.

Experimental studies of this kind can be carried out most simply in the case of the process of activated adsorption. As is known [10,13], the kinetics of activated adsorption on a heterogeneous surface — the process to which the statistical method has been most successfully applied — may be expressed, for defined conditions, by the approximate equation:

$$q(t) = q_\infty \int_{E_0}^{E=RT\ln k_0} \rho(E)dE \qquad (1)$$

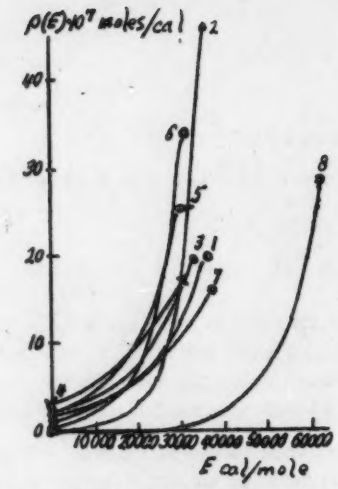

Fig. 1. Graph of the distribution function of surface area-elements for values of the adsorption activation energy of hydrogen on all the carbons studied: 1) ash-containing, 2) purified, 3) with 1% K added, 4) with 1% Ca added, 5) with 1% Pt added, 6) with 1% Ag added, 7) with 1% Ni added, 8) with 1% Fe added.

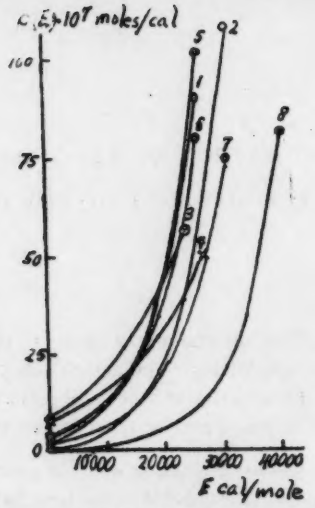

Fig. 2. Graph of the distribution function of surface area-elements for values of the adsorption activation energy of oxygen on all the carbons studied: 1) ash-containing, 2) purified, 3) with 1% K added, 4) with 1% Ca added, 5) with 1% Pt added, 6) with 1% Ag added, 7) with 1% Ni added, 8) with 1% Fe added.

where q is the amount of substance adsorbed up to the time t, q_∞ is the amount of adsorbed substance required to form a monomolecular layer on the surface; $\rho(E)$ is the distribution function of area-elements of surface according to value of the adsorption activation energy E, k_0 is the pre-exponential multiplier in the adsorption velocity constant, which is assumed constant over all area-elements; E_0 is the minimum value of the activation energy for the given surface. The function $\rho(E)$ is characteristic of a given adsorbent-adsorbate pair, and from a knowledge of this function, together with the value of k_0 it is possible to derive the kinetic equation for any temperature and pressure of the adsorbate.

The surfaces which have been most studied from the point of view of statistical theory are those of active carbons. The work of Roginsky and his coworkers [14, 10, 10] has shown that the surfaces of active carbons obtained from various sources are heterogeneous with regard to the adsorption activation energy of a number of gases.

Keier and Manko[19] made an experimental study of the effect of the natural ash in a number of technical birch carbons, and also the same carbons with the artificial addition of a series of mineral salts, on the nature of the surface distribution as shown by the adsorption activation energies of oxygen and hydrogen.

In all instances studied the distribution function was found to be of the exponential type,

$$\rho(E) = He^{\alpha E} . \qquad (2)$$

Figures 1 and 2 show graphs of the distribution functions determined by Keier and Manko [19] for the adsorption of oxygen and hydrogen on carbon of varying ash content and with different artificial additives. Differences in the distribution functions for different carbons and adsorbates result in different numerical values of the parameters H and α. However, these parameters are subject to fairly large variations, depending on the nature of the carbon and of the adsorbed substance (see Table 1).

Thus the presence in carbon of mineral constituents, as well as the nature of these constituents, affects the surface heterogeneity, as shown by the adsorptive properties of the carbon. This effect is reflected in a change in the distribution function for the energy of activation. How can this change be expressed? Different distribution functions

may be compared on the basis of type (linear, exponential, etc.). This is a purely qualitative comparison, however. Further, surfaces heterogeneous in regard to a given property, x, may be characterized by the range of the interval over which this property changes. If we compare among themselves a series of distribution functions, all of the same type $\rho(x)=H$ (uniform distribution), we see that in passing from ρ_5 corresponding to the least heterogeneous surface, to ρ_1, the most heterogeneous function, as shown in Fig. 3, the interval over which the property x for the given surface varies, increases with the degree of heterogeneity. Thus, in the case of a uniformly heterogeneous surface, a characteristic of the degree of heterogeneity is the range covering values of the parameter which has been selected as the independent variable. But in the case of other distributions this interval is not a well-defined characteristic. Indeed, if we compare the two distribution functions shown in Fig. 4, we see that, although both have the same range for the variable x, they differ in their degree of heterogeneity. The function ρ_1 represents a uniformly heterogeneous surface, but the function ρ_2 represents an almost homogeneous one, since the overwhelming majority of the area-elements of this surface have about the same value of the argument x.

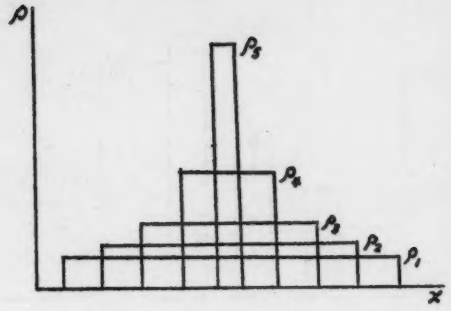

Fig. 3.

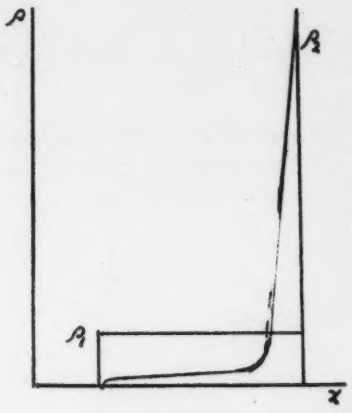

Fig. 4.

On the other hand, in this example (Fig. 3), because of the normal character of the distribution function, the value of the parameter H decreases as the interval for values of x increases Therefore, for a uniformly heterogeneous surface $\rho(x)=H$ the value of the distribution function H is a measure of the surface heterogeneity. The larger the value of H, the less heterogeneous the surface and the more it tends to homogeneity. In order to extend the treatment to any type of distribution, we consider a surface consisting of a series of uniformly heterogeneous area-elements, for each of which $\rho(x)=H_i$ (Fig. 5). The surface as a whole will be characterized by a mean value $\rho_i(x)$ which is obviously equal to

$$\overline{\rho}(x) = \sum_i \rho_i(x) \frac{s_i}{\sum_i s_i} \tag{3}$$

In this expression $\frac{s_i}{\sum_i s_i}$ is the fraction of the surface in the i-th uniformly heterogeneous area-element. For a surface with an infinite number of area-elements, i.e. for a smooth distribution function, (see Fig. 6), the ratio $\frac{s_i}{\sum_i s_i}$ is replaced by the product $\rho(x)dx$, which characterizes the fraction of area elements of the given type in the case of a smooth distribution function, and the sum (3) is replaced by the integral

$$\overline{\rho}(x) = \int_{x_1}^{x_2} \rho(x)dx\rho(x) = \int_{x_1}^{x_2} \rho^2(x)dx \tag{4}$$

The mean value of the distribution function obtained in this way may be used as a measure of heterogeneity for functions of any type. It is more convenient not to use $\overline{\rho}(x)$, but the reciprocal

$$\epsilon = \frac{1}{\overline{\rho}(x)}, \tag{5}$$

which we shall term "the degree of surface heterogeneity." By calculating the value of ϵ, we can compare the degree of heterogeneity of different surfaces.

We shall examine in what manner the degree of heterogeneity depends on the parameters of some concrete types of distribution function. In the case of the uniform distribution $\rho(x)=H$ the degree of heterogeneity, according to equation (5) will be equal to

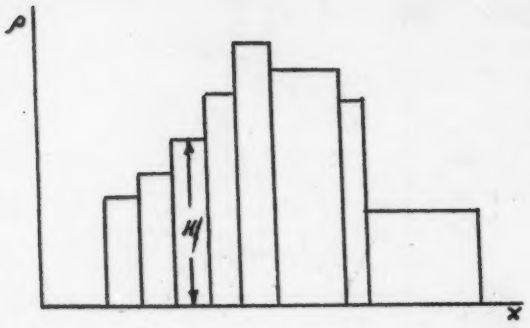

Fig. 5

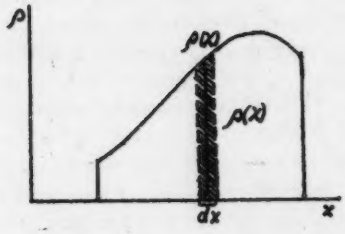

Fig. 6

$$\epsilon = \left[\int_{x_1}^{x_2} H^2 dx\right]^{-1} = \frac{1}{H^2(x_2 - x_1)} \tag{6}$$

But the difference $(x_1 - x_2)$, the interval over which the property x varies, depends in its turn on the quantity H, because of the normal character of the distribution function. Writing the conditions for normalization, we get

$$\int_{x_1}^{x_2} \rho(x)dx = \int_{x_1}^{x_2} H dx = H(x_2 - x_1) = 1,$$

from which

$$x_2 - x_1 = \frac{1}{H}$$

and consequently

$$\epsilon = \frac{1}{H} \tag{7}$$

Thus, for a uniform distribution the degree of heterogeneity is inversely propotional to the parameter H, which fully corresponds to Fig. 3.

In the case of an exponential distribution function $\rho(x) = He^{ax}$ we obtain the following expression for the degree of heterogeneity

$$\epsilon = \frac{2a}{H^2[e^{2ax} - e^{2ax_1}]} \tag{8}$$

Further, applying the conditions for normalization,

$$\int_{x_1}^{x_2} He^{ax} dx = \frac{H}{a}(e^{ax_2} - e^{ax_1}) = 1,$$

we get

$$e^{ax_2} = \frac{a}{H} + e^{ax_1} \tag{9}$$

From this the degree of heterogeneity will be equal to

$$\epsilon = \frac{2a}{H^2\left[\left(\frac{a}{H} + e^{ax_1}\right)^2 - e^{2ax_1}\right]} = \frac{2}{a + 2He^{ax_1}} \tag{10}$$

TABLE 1

Values of the distribution-function parameters for different carbon surfaces, as shown by the activation energies of hydrogen and oxygen

Carbon	$a \cdot 10^4$ mole/cal	$H \cdot 10^7$ mole/cal
Adsorption of hydrogen		
Sugar	3.00	—
Birch, deashed (ash content 0.4%)	1.93	0.07
" " plus 1% Ag	1.41	0.5
" " " 1% Fe	1.24	0.01
" " " 1% Pt	0.90	1.9
Birch (containing 3% ash)	0.74	1.4
Birch, deashed plus 1% K	0.72	2.0
1% Ca	0.60	3.0
1% Ni	0.59	1.9
Adsorption of oxygen		
Sugar	6.20	—
Birch, deashed (ash content 0.4%)	1.45	1.4
" " plus 1% Pt	1.43	2.9
" " " 1% Fe	1.40	0.3
Birch (containing 3% ash)	1.25	3.9
Birch, deashed plus 1% Ni	1.21	2.0
" " " 1% Ag	1.20	4.0
" " " 1% K	0.81	9.3
" " " 1% Ca	0.64	8.9

TABLE 2

Degrees of heterogeneity of different carbon surfaces for hydrogen and oxygen adsorption

Carbon	$\epsilon \cdot 10^{-4}$ cal/mole
Adsorption of hydrogen	
Sugar	0.67
Birch, deashed (ash content 0.4%)	1.03
" " plus 1% Ag	1.42
" " " 1% Fe	1.61
" " " 1% Pt	2.22
Birch (containing 3% ash)	2.70
Birch, deashed plus 1% K	2.77
" " " 1% Ca	3.17
" " " 1% Ni	3.40
Adsorption of oxygen	
Sugar	0.32
Birch, deashed (ash content 0.4%)	1.38
" " plus 1% Pt	1.40
" " " 1% Fe	1.42
Birch (containing 3% ash)	1.60
Birch, deashed plus 1% Ni	1.65
" " " 1% Ag	1.67
" " " 1% K	2.50
" " " 1% Ca	3.13

If $a \gg 2He^{ax_1}$, approximating, we may put

$$\epsilon = \frac{2}{a}, \tag{11}$$

i.e. the degree of heterogeneity is inversely proportional to the exponential index a.

By analogy with what precedes, the degree of heterogeneity of a power distribution function of the type $\rho(x) = H(x - x_1)^n$ may be expressed as follows

$$\epsilon = \frac{2n+1}{(n+1)^{\frac{2n+1}{n+1}}} \cdot \frac{1}{H^{\frac{1}{n+1}}} \tag{12}$$

From expression (10) for an exponential function, it follows that when $a = 0$ the degree of heterogeneity will be equal to $1/H$, as in the case of a uniform distribution, which is clearly obvious, since for $a = 0$ the exponential distribution $\rho(x) = He^{ax}$ reduces to the uniform distribution $\rho(x) = H$. As $a \to \infty$ the degree of heterogeneity reduces to zero, corresponding to an approach toward a homogeneous surface. In fact, when $a \to \infty$ the exponential function He^{ax} tends toward the infinite ordinate corresponding to a homogeneous surface.

In the same way, a power distribution reduces to a uniform distribution for $n = 0$ and to a narrow infinite peak, approximating to a homogeneous surface, for $n \to \infty$. In complete agreement with this the degree of heterogeneity ϵ becomes equal to $1/H$ (as for a uniform distribution) when $n = 0$, and tends to zero when $n \to \infty$.

Thus, for a surface having an arbitrary type of distribution the degree of heterogeneity may vary (for a fixed interval of change of the argument $\underline{x}$) from 1/H, corresponding to a uniformly heterogeneous surface, to zero, corresponding to a surface approaching homogeneity. And in turn the degree of heterogeneity for a uniformly heterogeneous surface may vary from zero ($H \rightarrow \infty$) (homogeneity) to an indefinitely large quantity ($H \rightarrow 0$).

By calculating the value of ϵ, obtained in Equation (5), we can make comparisons between distributions both of the same and of different types with regard to their degree of heterogeneity.

We shall use the method described to determine the degree of heterogeneity of the carbons with different constituents, investigated by Keier and Manko [19]. Calculation shows that for all the samples the inequality $He^{\alpha E_0} \ll \alpha$ is valid; consequently, we may calculate the degree of heterogeneity by the approximate formula (11), making use of the values of α given in Table 1.

The values of the degree of heterogeneity for the adsorption of hydrogen and oxygen on the carbons studied by Keier and Manko [19] are given in Table 2. The data in this table show that the presence of extraneous constituents in the carbons is reflected in the degree of heterogeneity, and this varies with the nature of the constituent and the adsorbed substance.

Comparing the degree of heterogeneity of the carbon "BAU", which contains 3% of ash, with that of the same carbon after its ash content has been reduced by special treatment to 0.4%, we see that in the second case the degree of heterogeneity ϵ is lower both for hydrogen and for oxygen adsorption. The degree of heterogeneity is still lower in the sugar carbons, which have an ash content of a lower order than that of the "BAU" carbon. (Table 3). Thus, the degree of heterogeneity of the carbon, as shown by the adsorption activation energy, increases with the natural ash content.

The degree of heterogeneity is influenced not only by the presence of natural ash, but also by the artificial addition of metals. As will be seen from Table 2, the addition to "BAU" deashed carbon of silver, iron, platinum, calcium or nickel causes an increase in the degree of heterogeneity, though the effect varies with the nature of the additive and with the gas adsorbed. The degree of heterogeneity of sugar carbons also is increased by the introduction of additives, as is shown by Table 4, which has been compiled from the data of Burshtein [20] and of Keier and Manko [19].

TABLE 3

Degree of Heterogeneity of Carbons of Different Ash Content as Shown by Adsorption of Hydrogen and Oxygen

Carbons	Ash content, %	$\epsilon \cdot 10^{-4}$ cal/mole	
		Hydrogen adsorption	Oxygen adsorption
Sugar	0.05	0.67	0.32
Birch, deashed	0.4	1.03	1.33
Birch containing ash	3.0	2.70	1.60

The correlation between the degree of heterogeneity and the amount of extraneous constituents present, which is observed in the case of natural ash constituents, is also found when the extraneous constituents are introduced artifically. Table 4 shows that the degree of heterogeneity of deashed "BAU" carbon with added calcium increases with the calcium content, and the degree of heterogeneity of sugar carbon increases with the platinum content.

The data presented here are not sufficiently extensive to establish a relationship between the degree of heterogeneity and the quantity of extraneous constituent. However, it is clear that the relationship is not a linear one. For low concentrations of the additive (or extraneous constituent), the rate of increase in the degree of heterogeneity is greater than the rate for high concentrations.

Thus, the presence of extraneous additives in carbon affects the degree of surface heterogeneity, causing an increase in all cases. This effect of additives is not peculiar to the adsorption of hydrogen and oxygen, but also occurs with other gases, as will be seen from Table 4, which gives values (calculated from the data of Burshtein [20]) of the degree of heterogeneity for the adsorption of carbon monoxide on sugar carbon, both with and without the addition of 0.2% of platinum.

The degree of heterogeneity of a surface for a given gas is evidently a fairly constant characteristic. The degree of heterogeneity for the adsorption of oxygen on birch carbon (calculated from the data of Reed and Wheeler [21]) was found to be fairly close to the value obtained from the data of Keier and Manko [19] (Table 5). In the case of hydrogen adsorption, values of the degree of heterogeneity calculated from the data of Keier and Roginsky are fairly close to similar values calculated from the data of Burshtein (Table 5).

TABLE 4

Degrees of Surface Heterogeneity of Sugar and Birch Carbons with Various Amounts of Different Additives

Hydrogen adsorption		Hydrogen adsorption*		Carbon monoxide adsorption*	
Carbons	$\epsilon \cdot 10^{-4}$ (cal/mole)	Carbons	$\epsilon \cdot 10^{-4}$ (cal/mole)	Carbons	$\epsilon \cdot 10^{-4}$ (cal/mole)
Deashed birch	1.03	Sugar	0.73	Sugar	0.67
Deashed birch plus 0.01% Ca	2.00	Sugar plus 0.02% Pt	0.96	Sugar plus	
Deashed birch plus 0.1% Ca	3.30	Sugar plus 0.2% Pt	0.83	0.2% Pt	1.2
Deashed birch plus 1.0% Ca	3.34	Sugar plus 1.0% Pt	0.83		

* Data of Burshtein [20]

TABLE 5

Degrees of Surface Heterogeneity of Sugar and Birch Carbons for the Adsorption of Hydrogen and Oxygen, According to Data from Various Sources

Gas adsorbed	Carbon	$\epsilon \cdot 10^{-4}$ (cal/mole)	Reference
Hydrogen	Sugar	0.67	Keier and Roginsky
		0.73	Burshtein [18]
Oxygen	Birch	1.82	Reed and Wheeler
		1.60	Keier and Manko

This analysis of the experimental data on the kinetics of activated adsorption confirms the hypothesis put forward earlier, according to which there is a connection between surface heterogeneity and the presence of secondary constituents on the surface. Since in all cases the introduction of new constituents or an increase in the amount of those already present results in an increase in the degree of heterogeneity, the presence of these constituents is evidently a fundamental cause of heterogeneity. From this point of view it is clear why all the adsorbents investigated were found to be heterogeneous in their adsorptive properties, since it is difficult to imagine the surface of a real solid body completely free of extraneous constituents.

The constancy of distribution type, which was found to be exponential in all cases, is noteworthy. The same type of distribution occurs with carbons containing natural ash, with carbons freed from ash, and with carbons containing artificial additives. The same type of exponential distribution is characteristic of both sugar and birch carbons. Analysis of the data obtained by various authors with various samples at different times points to an exponential distribution of active centers, as shown by the activation energy for activated adsorption. This holds for hydrogen and for oxygen adsorption, and also for the adsorption of other gases, and not only for carbon but also for other adsorbents. This constancy of statistical surface characteristics suggests that there exists some property which is common to all, or most, adsorbents. From what has been said above, this property must be connected with the presence of secondary constituents on the surface.

The insensitivity of distribution type to the nature of the extraneous constituent suggests that for a wide range of substances, the same mechanism governs the action of the extraneous constituent on the distribution, irrespective of the nature of the constituent. In particular, it may be supposed that there is a connection between the distribution of active centers according to activity values and the distribution of individual inclusions according to their size. Moreover, there should be a connection between the inclusion size for a given extraneous constituent and the energy of activated adsorption (as the main characteristic of activity) on the adsorption center associated with this inclusion. With this assumption the constancy of distribution type for the activation energy points to a constant type of distribution for the extraneous constituents, according to the size of the inclusions. The parameters of the latter distribution will vary with variations in the concentration of the constituent, though the distribution type remains unaltered, in the same way as distributions based on the law of chance (Poisson-Gauss distributions). And there will be corresponding variations in the parameters of the distribution for the activation energy.

SUMMARY

1. A method is proposed for the quantitative evaluation of the degree of heterogeneity of distributions which is applicable to distributions of any type.

2. It is shown that the degree of surface heterogeneity of active carbons, as shown by the activation energy for activated adsorption, is dependent on the nature and on the quantity of the secondary constituents. In all cases an increase in the quantity of these constituents results in an increase in the degree of surface heterogeneity.

The secondary constituents have no effect on the distribution type.

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A STUDY OF THE CONDITIONS FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF SILICIC ACID

COMMUNICATION I. METHODS OF DETERMINING SILICIC ACID IN SILICATES BY DEHYDRATING SOLUTIONS OF THE ACID

E. N. Egorova

The gravimetric determination of silicic acid separated from acid solutions is one of the oldest analytical methods. There is an extensive literature on the study of the conditions for the separation of silicic acid from solutions. But, in spite of the large amount of experimental work in this field, the conditions for the complete separation and accurate determination of silicic acid have not been completely elucidated. Many examples of significant errors in the determination of silicic acid, carried out both by classical and by rapid methods, are to be found in practice. These errors occur even when the analytical procedure is technically unimpugnable. The obscurity surrounding the sources of the errors is reflected, evidently, in the different variants of the analytical procedure recommended by different authors.

The generally accepted "classical" method for the determination of silica in silicates consists, as we know, of the following operations:

1. The finely ground silicate sample is fused with sodium carbonate, or with a mixture of sodium and potassium carbonates, and the melt is decomposed with acid, or the sample is directly decomposed by acid, if the silicate is one of those amenable to this treatment. In the decomposition of the melt, variations may be made in the choice of acid and in its concentration. A number of authors prefer to decompose the melt with acid of high concentration [1,2], but others regard this point as unimportant [3,4,5]. Hydrochloric acid is most often recommended, but sometimes nitric acid, sulfuric acid, or perchloric acid is preferred.

2. Evaporation to dryness of the solution obtained and drying of the residue in order to achieve the maximum dehydration of the separated silicic acid and to convert it into the slightly-soluble form. Drying is carried out either by maintaining the residue in a dish on a boiling water-bath, the heating time not being precisely specified by the methods, or it is recommended that the residue should be dried in a thermostat at a temperature of 105-120° and higher.

Evidently, the nature of the salts present in the residue and their proportions, and also the nature of the dish, whether platinum or porcelain, in which the operation is carried out are not matters of indifference. Platinum is preferred because the transference of the separated silicic acid to the filter is more easily effected with a platinum dish than with a porcelain one; on the other hand, with a porcelain vessel a small increase in the weight of the silicic acid, due to corrosion of the vessel by acid, is unavoidable; it is generally considered that with porcelain vessels these two sources of error compensate one another, since they cause errors opposite in sign. In addition to this the conditions of drying on a boiling water bath with platinum and with porcelain vessels are not strictly comparable.

3. Treatment of the dried residue with concentrated acid in order to dissolve basic salts of iron, aluminum, titanium, and other metals, followed by extraction of the dry residue with water to bring the salts into solution. According to the existing procedures, the digestion of the dry residue with acids and the extraction of the salts may be carried out in different ways; both the quantity and the concenration of the acid may vary, as well as the time of digestion and the temperature at which the operation is carried out.

4. Filtration and washing of the residual insoluble silicic acid. The washing of the silicic acid is of essential importance for completeness of separation. There is no agreement as to how this operation should be carried out. It is recommended that the residue of separated silicic acid should be washed with water, or with acid solutions of different concentrations or even with ammonium nitrate solution; the recommended temperatures for the washing liquid also vary. It is not made sufficiently clear in the literature to what degree the silicic acid is reversibly dissolved in the washing liquid when the precipitate is being washed and what factors have a significant effect in this process.

5. Separation of silicic acid remaining in solution by a second evaporation of the filtrate and repetition of the operations described above.

6. Ignition of both silicic acid precipitates to constant weight, treatment of the silica with hydrofluoric

and sulfuric acids (as a check), evaporation of the acids, ignition and weighing of the non-volatile residue. This operation is generally carried out in the same way; the ignition temperature must be high.

7. Separation of silicic acid from the trioxides, its ignition to constant weight, and control treatment with hydrofluoric and sulfuric acids.

It is known that silicic acid is not completely separated by the two-stage evaporation of acid solutions. The silicic acid remaining in solution is brought down with the tri-hydroxides when ammonia is added to precipitate these. The separation of the silicic acid from the trioxides is the seventh, or last, of the analytical operations described above. This operation is not always carried out by analysts because it is generally considered that the two-stage evaporation of the solution results in almost complete separation of the silicic acid, the amount remaining in solution being small enough to be neglected. However, the results obtained by several workers show that the trioxide precipitate often contains significant quantities of silicic acid [6, 7]. The separation of silicic acid from the R_2O_3 precipitate is carried out either by dissolving the oxides in sulfuric acid or by fusing them with potassium pyrosulfate.

Thus, there is no uniform procedure for carrying out the "classical" method for the separation and gravimetric determination of silicic acid. Although the method has been repeatedly studied, there is no uniform procedure for carrying out the operations in the analytical literature or in the text-books on silicate analysis. And variants which differ still more widely are used in laboratories which carry out silicate analyses. The greater part of the work on the study of the separation of silicic acid by evaporating solutions is devoted to two operations of the method, namely, the dehydration of the residue obtained by evaporating the acid solution, and the washing of the separated silicic acid; these two operations are the object of special interest on the part of investigators.

In studying the dehydration conditions investigators have paid great attention to the temperature at which the residue of salts is dried, from the point of view of obtaining a complete separation of silicic acid and a residue of high purity. Investigators differ in their opinions as to what is the best drying temperature. In a text book on the analysis of minerals [3], it is recommended that the residues from the first and second evaporations should be dried entirely on a boiling water bath; this temperature is considered sufficient to convert the silicic acid into the difficultly soluble state.

The work of Gilbert [8] has also shown that dehydration of the dry salts in a thermostat at a temperature above 100° has no advantages over dehydration on a boiling water bath insofar as complete separation of silicic acid is concerned. However, a number of investigators recommend, on the basis of their own work, that the dehydration should be effected at a temperature of 105-120°, as they consider that a more complete separation of silicic acid is achieved by the use of such a temperature [9, 10, 11]. As a result of this work, Hillebrand and Lundel [4] and Kolthoff and Sandell [5] recommend that the residue from the second evaporation be dehydrated at 105-110°. Finally, several methods stipulate the still-higher dehydration temperature of 140° [12, 13, 14].

In most cases studies on the relation between dehydration temperature and completeness of separation of the silicic acid have been carried out on natural or on technical silicates, i.e., with silicic acid separated from solutions containing various salts. More attention has been devoted to the effect of dehydration temperature than to the effect of various salts on completeness of separation. The problem of contamination of the separated silicic acid by various impurities in relation to the dehydration temperature employed is the one which has been most studied.

Gilbert [8], in the course of analyses on fireproof materials and feldspars, studied the effect of dehydration temperature on the completeness of separation of silicic acid and on its purity when significant quantities of aluminum, calcium, and magnesium salts are present. According to his results, the presence of calcium or aluminum does not increase the amount of silicic acid which goes into solution even when the dehydration temperature is as high as 280°; but as a result of the formation of magnesium silicate which is decomposed by hydrochloric acid, the presence of magnesium causes an increase in the silicic acid solubility, even when the dehydration temperature is as low as 120°. On determining the purity of the silicic acid separated at the higher dehydration temperatures, the author found no calcium, but with the same dehydration conditions small amounts (tenths of a milligram) of magnesium were detected.

Jordis [15] studied the analysis of barium, strontium, and calcium silicates, which are decomposed by hydrochloric acid. His work showed that the separation of silicic acid is least complete in the analysis of calcium silicate, a more complete separation being achieved with barium and strontium silicates. However, as a criterion of completeness the author uses the sum of the percentages of SiO_2 and basic oxide, which is close to 100%. In addition, in the filtrate after separation of SiO_2 and basic oxide (BaO) the author found a residue

amounting to 2% (instead of the calculated deficiency of 0.14%), which he attributed to "impurities". For this reason the author's results must be held in doubt.

Jordis and Ludewig[13] in studies on calcium, strontium and barium silicates, decomposed by acids, used special conditions for the separation of silicic acid from solution in order to show more clearly the relationship between its solubility and the presence of these cations. In the dehydration, they achieved a more complete removal of HCl by boiling the residue twice in succession with water and heating until the odor of HCl had completely disappeared. Under these conditions the solubility of the dehydrated silicic acid was greatly increased, and the effect showed a progressive increase, in the order barium to calcium. Under the same conditions, the presence of alkali salts caused a still greater increase in the silicic acid solubility.

Lenher and Troug [16] studied the effect of dehydration temperature on contamination of the separated silicic acid, the acid being separated from solutions containing salts of calcium, magnesium, and iron. The authors' results show that, in the presence of calcium the silica separated is only slightly contaminated with this metal, although a dehydration temperature of 150° was employed. This conclusion agrees with the results given by Hillebrand [17], who also found no calcium in the SiO_2 obtained in the analysis of various silicates. According to Lenher and Troug, when silicic acid is dehydrated in the presence of magnesium at temperatures higher than 115°, marked "contamination" of the residue with magnesium takes place. In the presence of iron, the silicic acid separated always contained significant quantities of this metal even in those cases where the dehydration temperature did not exceed 110°.

The amount of silicic acid which passes into solution when the precipitate is treated with solutions of varying composition depends to a large extent on the washing process. This problem has also been the subject of a number of investigations. The most complete study of the solubility of silicic acid in solutions of hydrochloric and sulfuric acid of varying concentration is that of Lenher and Merrill [18]. According to their results, the silicic acid solubility increases as the concentration of hydrochloric or sulfuric acid in the washing liquid decreases, maximum solubility being reached with pure water. It was also shown that the solubility increases with temperature. The numerical results given by these authors were obtained under conditions which ensured that equilibrium was attained (i.e., on saturated solutions of silicic acid). They showed that at a temperature of 25° the equilibrium state is reached in a few days, and at 90°, in a few hours.

The data obtained are of interest, but it is utterly impossible to draw analytically useful conclusions from them, because the conditions under which the solution acts on the silicic acid in the analytical process are entirely different from those under which the authors conducted their experiments. However, the characteristics of the dissolution process, i.e., dependence of silicic acid solubility on the concentration of mineral acid and the effect of temperature on solubility, are obviously valid under analytical conditions.

Lenher and Troug [16] showed that when dehydrated silicic acid was treated with concentrated, with 20%, and with 10% hydrochloric acid, the maximum loss occurred with the 10% acid; treatment with 20% acid gave results close to those obtained with the concnetrated acid. The same authors showed that when dehydrated silicic acid was washed with solutions of HCl, NaCl, and NH_4Cl, and also with water, the greatest loss was found with NH_4Cl solution, a smaller loss with NaCl solution, and the minimum loss with water. Bucherer and Meier [9] studied the effect of washing silicic acid, which had previously been washed free of chloride ions, with hydrochloric acid of different concentrations; they showed that the minimum loss occurred with 10% HCl, a greater loss with 15%, and the maximum loss with 20% HCl. These results are not in accord with the data of investigators already cited.

Hawley [12], studying the loss of dehydrated silicic acid by dissolution, concluded that its solubility is at a maximum in 15-25% solutions of hydrochloric acid; with higher or lower concentrations of hydrochloric acid the solubility decreases (the author gives concentrations in volume percentages; the calculated weight percentages corresponding to these are 6.5-11%). According to the author, the solubility in pure water is extremely low, but it is greatly increased in the presence of sodium chloride. All the authors cited determined the qua quantity of dehydrated silicic acid passing into solution by evaporating the wash-water, dehydrating the dry residue, and treating it so as to remove the silicic acid by filtration, i.e., in a manner which, in our opinion, makes complete separation impossible.

In view of the contradictory results obtained by various authors cited above, we carried out an experimental study in order to elucidate the effect of dehydration temperature and the effect of the nature of washing solutions on the completeness of separation of silicic acid from solutions used in its analytical determination.

EXPERIMENTAL

A series of dehydration experiments was carried out at different temperatures in order to find the effect of

temperature and of duration of dehydration on the completeness of separation of silicic acid. A sample of amorphous chemically pure silica, which had been previously heated to constant weight, was used as starting material in all the experiments. Its purity was first checked by treatment with hydrofluoric and sulfuric acids. The non-volatile residue obtained by calcining the silica amounted to 0.1%. The content of non-volatile impurities (0.1%) was taken into account in calculating the sample weights for individual experiments. The sample weight amounted to 0.3-0.4 g. The sample was fused with a six-fold quantity of Na_2CO_3, the melt extracted in a platinum dish with water and decomposed with concentrated hydrochloric acid. The acid solution was evaporated to dryness and the dehydration carried out at different temperatures. The dehydrated gel was treated with 5 ml of concentrated hydrochloric acid for 5 minutes, and after dilution to about 50 ml with water, the solution was maintained on a boiling water bath for 10-15 minutes to dissolve salts (NaCl). The separated silicic acid was removed by filtration and washed with hot dilute hydrochloric acid (in some experiments) or with water. The filtrate was evaporated a second time and after dehydration of the dry residue under the same conditions a second silicic acid precipitate was obtained.

The silicic acid precipitate from the second evaporation was washed either with dilute hydrochloric acid (1: 99) or water (in those cases in which hot water was used to wash the main precipitate from the first evaporation). Both silica precipitates were ignited to constant weight. The ignited silica was checked for purity by treatment with mixed acids ($HF + H_2SO_4$).

The results obtained by dehydrating silicic acid at 100° are given in Table 1.

TABLE 1

Expt. No.	Separation conditions			SiO_2 found as percent of quantity taken
	Dehydration		Composition of washing solutions*	
	Temperature (°C)	Hours heated		
1	On boiling water bath	3	Hot water	99.13
2	"	3	"	99.43
3	"	3	"	99.58
4	"	1	"	99.77
5	"	1	"	99.69
6	"	1	"	99.62
7	"	1	Hot solution of HCl (5: 95)	99.32
8	"	1	"	99.73
9	"	1	"	99.20
10	"	1	"	99.15
11	"	1	"	99.51
12	"	1	"	99.12
13	In thermostat at 98-100°	1	"	99.37
14	"	1	"	99.37
15	"	1	"	99.51
16	"	1	"	99.22
17	"	1	"	99.21
18	"	1	"	99.20
19	"	1	"	99.60
20	"	1	"	99.67

* This solution was used for washing the main silicic acid mass (first separation). The silicic acid obtained in the second separation was washed with dilute hydrochloric acid solution (1: 99).

TABLE 2

Expt. No.	Separation conditions		SiO_2 found as percent of quantity taken
	Dehydration temperature (°C)	Composition of washing solution	
1	108-110	Hot solution of HCl (5: 95)	99.41
2	108-110	"	99.79
3	108-110	"	99.80
4	108-110	"	99.71
5	108-110	"	99.79
6	108-110	"	99.43
7	108-110	"	99.68
8	108-110	"	99.62
9	108-110	"	99.51
10	108-110	"	99.55
11	108-110	"	99.52
12	108-110	"	99.65
13	108-110	"	99.60
14	108-110	"	99.62
15	108-110	"	99.76*
16	108-110	"	99.73*
17	114-120	"	99.86
18	114-120	"	99.27
19	114-120	"	99.52
20	114-120	"	99.52
21	114-120	"	99.77

* Melt decomposed by HCl (1: 1)

As will be seen from these figures, whether dehydration is carried out for one hour or for three hours makes no material difference in the quantity of silicic acid separated. The quantity of silicic acid separated amounts on the average to 99.43% of SiO_2 based on the amount of SiO_2 taken (mean of 20 determinations).

The deviations between the individual determinations lie within the limits 99.12-99.77%. When the silicic acid obtained under identical dehydration conditions was washed with different washing solutions—dilute hydrochloric acid and water—there was no material difference in the SiO_2 results obtained.

In the next series of experiments the dehydration was carried out at higher temperatures, namely 108-110° and 114-120°, for one hour. The results obtained are given in Table 2.

When the dehydration temperature is raised to 110° the quantity of silicic acid separated is slightly greater, and the deviation between individual SiO_2 determinations less, than that found when the dehydration is carried out at a temperature of about 100°. The mean value for the SiO_2 found is 99.61%, and the deviations between duplicate experiments lie within the limits 99.41 and 99.80%.

In experiments 15 and 16, the melt was decomposed with HCl (1:1) and good agreement was obtained between duplicates (99.73-99.76). The higher dehydration temperature of 114-120° does not, it appears, increase the quantity of silicic acid separated—the mean SiO_2 content from five determinations is 99.58%, and deviations between duplicates lie within a range of 0.5%.

In order to find the effect of the composition of the solution on completeness of separation, we carried out experiments on the separation of silicic acid from hydrochloric acid solutions which contained considerable amounts of sodium chloride, the chlorides of calcium, magnesium, titanium, and aluminum being also present. The dehydration was effected on a boiling water bath for one hour. In each experiment a weighed sample of the appropriate oxide was added to the sample (0.3-0.4 g) of chemically pure SiO_2, previously ignited to constant weight. The mixture of oxides was fused with sodium carbonate. The melt was decomposed with HCl (1:1). The results are given in Table 3.

TABLE 3

Expt. No.	Weight, in g					SiO_2 found as percent of quantity taken		
	CaO	MgO	TiO_2	Al_2O_3	SiO_2 : RO_n (weight)	Separation 1	Separation 2	Total
1	0.086	—	—	—	4.3	99.08	0.92	100.00
2	0.086	—	—	—	3.7	99.21	0.70	99.91
3	0.170	—	—	—	2.1	98.97	1.03	100.00
4	0.170	—	—	—	2.1	99.32	0.68	100.00
5	—	0.055	—	—	5.6	98.41	0.70	99.11
6	—	0.055	—	—	5.6	98.36	0.96	99.32
7	—	0.110	—	—	3.1	98.85	0.65	99.50
8	—	0.110	—	—	2.9	98.53	1.12	99.65
9	—	—	0.025	—	14.7	99.13	0.60	99.73
10	—	—	0.025	—	14.0	99.26	0.51	99.77
11	—	—	0.031	—	11.4	98.70	0.96	99.66
12	—	—	0.031	—	12.4	98.54	1.15	99.69
13	—	—	0.015	—	20.4	98.79	0.98	99.77
14	—	—	—	0.160	2.4	—	—	99.90
15	—	—	—	0.160	2.0	—	—	100.09

As these results show, the presence of calcium or aluminum promotes more complete separation of SiO_2. This agrees with the work of Gilbert, but is not in accord with the results obtained by Jordis and by Jordis and Ludewig. It should be mentioned that Jordis carried out his investigations on calcium silicates, which are decomposed by acids, in the presence of alkali salts. It is possible that under these conditions the silicic acid is not sufficiently dehydrated. We know that in the decomposition of carbonate rocks the soluble silicic acid obtained is difficult to dehydrate by evaporating acid solutions in the presence of considerable quantities of calcium chloride. Further studies by these authors (Jordis and Ludewig) are not comparable with our results because of the material changes which they made in the analytical conditions.

Our results show that the presence of magnesium (Expts. 5-8), slightly reduced the amount of silicic acid separated, though the dehydration temperature was not above 100°. In these experiments the non-volatile residue obtained after treatment of the ignited silica contained magnesium in amounts corresponding to 0.4-0.2 mg of MgO. The presence of titanium (Expts. 9-13), apart from causing significant contamination, had no marked influence on the completeness of separation.

Investigation of the effect of dehydration temperature on completeness of separation of the silicic acid from solutions showed that variations in temperature (above 100°) had comparatively little effect on the quantitative separation of SiO_2. Nevertheless, when the silicic acid was dehydrated at a temperature close to 100°, slightly lower average values for SiO_2 were obtained. It should also be mentioned that in our experiments, platinum vessels were used, and under these conditions when the dry residue is heated on a boiling water bath the dehydration temperature is close to 100°. When porcelain vessels are used under the same conditions, the dehydration will take place at a lower temperature, and it is possible that still lower SiO_2 values will be obtained. When porcelain vessels are used, it is therefore advisable to carry out the dehydration in a thermostat at 108-110°. A higher temperature (118-120) will not increase the quantity of silicic acid separated, but if magnesium salts are present, it will increase the loss of silicic acid when the dry residue is later treated with acid solutions.

In order to determine to what extent the separated silicic acid passed into solution, we carried out experiments in which it was washed with hot water and with dilute hydrochloric acid solutions. In these experiments we made separate determinations of the silicic acid separated by dehydration, the silicic acid in the main filtrate, and the silicic acid in the washing-liquids, which were collected separately. There are two possible sources of the silicic acid in the main filtrate: it may be due either to incomplete conversion of silicic acid to the difficultly-soluble form in the course of dehydration, or to reversible solution of this form when the dry residue is treated with an acid solution containing considerable quantities of sodium chloride. There are many references in the literature to the enhanced solubility of silicic acid in the presence of alkali metal chlorides, but at present it is not possible to say which of these causes is of the greatest significance.

The amount of silicic acid in the main filtrate and in the washing liquids, the volume of which was 300 ml in all the experiments, was determined by precipitating the silicic acid with aluminum hydroxide. We used artificial solutions to work out the method of separating silicic acid by coprecipitation. The amount of alumina required for the quantitative separation of silicic acid from solution by coprecipitation with aluminum hydroxide was determined from experimental data.

In all the experiments carried out the conditions used for the dehydration and digestion of the silicic acid were identical. The weighed sample of calcined SiO_2 (chemically pure) was fused with 2 g of Na_2CO_3. The melt was decomposed on a platinum dish with 20 ml of HCl (1: 1), and the solution was evaporated to dryness on a boiling water bath. The dry residue was ground with a glass pestle and dehydrated for an hour at a temperature of 105-110°. The cooled dry residue was moistened with 5 ml of concentrated hydrochloric acid and the dish was allowed to stand covered with a watch glass for 2-3 minutes, after which 45 ml of water was added and the covered dish placed on a water bath for 10 minutes to dissolve the salts. The silicic acid separated was removed by filtration. The main filtrates were collected separately from the washing liquids.

TABLE 4

Expt. No.	SiO_2 found, as % of quantity taken			
	Separated by dehydration	In main filtrate	In washing liquids	Total
1	98.54	0.63	0.89	100.06
2	98.59	0.77	0.69	100.03
3	98.97	0.45	0.53	99.95
4	98.53	0.55	0.80	99.88
5	98.56	0.58	0.77	99.91
6	98.01	0.95	1.00	99.96
7	97.43	0.96	1.48	99.92
8	98.04	0.77	1.34	100.15

Note. In Experiments 1-3 the separated silicic acid was washed with hot dilute hydrochloric acid (5: 95); in Experiments 4-6, with hot water, and in Experiments 7-8 with hot 10% HCl solution.

In Experiments 1-3 the separated silicic acid was washed with hot dilute hydrochloric acid (5: 95), in Experiments 4-6 with hot water, and in Experiments 7-8 with hot 10% HCl solution. In all the experiments the volume of the washing liquid was the same, 300 ml. The results obtained are given in Table 4.

The results obtained show that:

1. The total amount of SiO_2 found in all the experiments is close to 100%, from which it follows that there were no notable silicic acid losses.

2. The quantity of silicic acid in the main filtrate obtained after separating the bulk of the silicic acid varied within wide limits in replicate experiments: the limits were 0.45 to 0.96% (based on the amount taken). This suggests that, in spite of identical dehydration conditions and relatively close absolute weights of the silicic acid starting material (0.33-0.41 g), the amount remaining in solution may vary, i.e., completeness of precipitation is determined by other, unknown factors. It seems to us that an important factor here is the degree of polymerization of the silicic acid in the operations preceding dehydration.

3. When hot dilute hydrochloric acid (5: 95) was used as the washing liquid, the amount of silicic acid

dissolved in it was 0.53 to 0.89%. With hot water a somewhat larger amount was lost (0.77-1.00%). With hot 10% HCl solution a still greater loss was observed (1.48-1.34%). For this reason, hot, very dilute solution of hydrochloric acid (5: 95) is recommended for washing the precipitate of silicic acid separated from hydrochloric acid solutions.

SUMMARY

1. A study was carried out on the effect of dehydration conditions (time and temperature of dehydration, presence of salts) and of washing processes on the completeness of separation of silicic acid from solutions.

2. It has been shown that the completeness of separation by dehydration depends not only on the choice of conditions of dehydration, washing, and other analytical factors usually regarded as significant, but also on some unknown factors; it is suggested that completeness of separation of silicic acid depends on the degree of polymerization of the silicic acid produced in the treatment which precedes dehydration of the salts.

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STUDY OF THE "COMPOSITION – HEAT-STRENGTH" DIAGRAM FOR ALLOYS OF THE QUATERNARY SYSTEM IRON – CHROMIUM – NICKEL – MANGANESE

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In recent years [1,2] systematic studies have been carried out by the centrifugal method on the strength of metallic alloys at high temperatures. Up to the present, studies by this method have included alloys of a number of binary systems, Al–Mg, Mg–Cd, Ni–Cr [3,4], and alloys of the ternary system, Fe–Cr–Ni [1], corresponding to continuous or limited solid solutions of these systems. In these studies some relationships have been established between phase nature and structure and the character of the "composition – heat-strength" diagrams

There are no references in the literature to systematic studies of the "composition – heat-strength" diagrams for alloys of the quaternary system iron – chromium – nickel – manganese. The authors have studied the diagram of this system over the past few years.

EXPERIMENTAL

In the present paper experimental results obtained in a study of the electrical resistance, hardness at room temperature, and heat-strength at 800° of alloys of one section of this quaternary system are given. The basic section used was that of the ternary system iron – chromium – nickel, passing from the chromium corner to the binary system iron – nickel with iron and nickel in constant (1:1) proportions; its apex corresponds to the apex of the tetrahedron representing a manganese content of 100%.

Fig. 1 represents part of this section for a temperature of 800°. The boundary of the γ solid solution marked here on the ternary iron – chromium – nickel side was drawn from data given in the literature [5]. Data obtained from experimental studies of microstructure, hardness, and specific electrical resistance on alloys tempered at 800° were used in constructing the boundaries at the ternary iron – nickel – manganese side, as well as at other parts of the quaternary system. After casting, all of the alloys were subjected to homogenizing annealing treatment for 48 hours at 1100°, slow cooling in the furnace to 800°, and tempering at that temperature.

Not all the two-phase and three-phase regions adjacent to the solid solution were studied in detail, and for this reason some of them are denoted on Fig. 1 by dotted lines. The alloys situated close to the boundary of the solid solution were chemically analyzed. The analyses showed only insignificant deviations in composition from the figures obtained by calculation. Most of the alloys were therefore not subjected to chemical analysis.

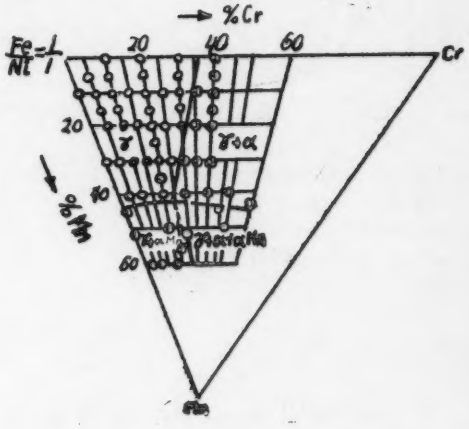

Fig. 1. Isothermal section of the quaternary system at 800°: ○ – one phase; ● – two phases; ◉ – three phases.

Fig. 2 shows the relationship between specific resistance and composition for alloys of this section tempered at 800°. Here each curve represents alloys of constant manganese content, the proportions of the other components varying. The change in the course of a curve corresponds to a change in the phase composition of the alloys – from the single-phase region of the γ solid solution to the two-phase region, γ + α, and this was confirmed by microanalysis. It is noteworthy that the specific resistance of the γ solid solution remains almost constant when its chromium content varies; and an increased manganese content has little effect here. Transition from the γ solid solution to the two-phase region, γ + α, is accompanied by a significant increase in hardness.

The diagram composition – heat-strength for the alloys of the section considered was studied by measuring the bending deflection of samples under the action of centrifugal force [1]. Cast samples, 80 mm long and 3.85 mm in diameter, were first annealed for 48 hours at 1100° and then subjected to bending for definite periods of

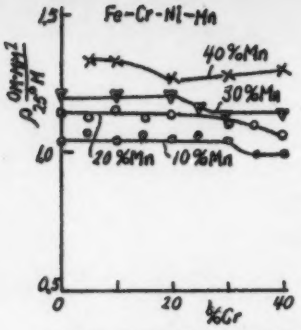

Fig. 2. Specific electrical resistance of quaternary alloys tempered at 800° in relation to composition.

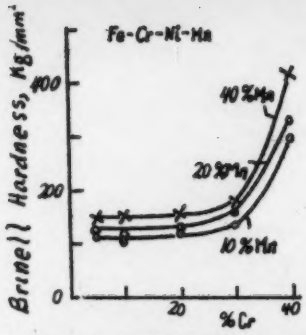

Fig. 3. Hardness of quaternary alloys tempered at 800° in relation to composition: ● – 10% manganese; o – 20% manganese; x – 40% manganese.

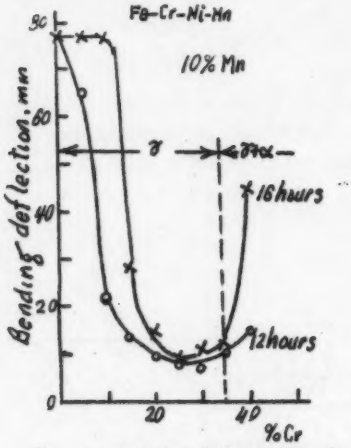

Fig. 4. Relation between bending deflection of quaternary alloys at 800° and chromium content (10% manganese).

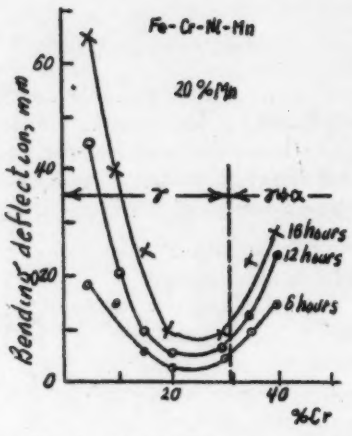

Fig. 5. Relation between bending deflection of quaternary alloys at 800° and chromium content (20% manganese.

time (6, 12, and 16 hours) at 800°; after each period, the bending deflection was measured. The initial deformation stress chosen was 2.78 kg/mm².

Curves showing the dependence of bending deflection on the chemical composition of the alloys are given in Figs. 4, 5, and 6. These show that for a given manganese content the bending moment of alloys from the region of γ solid solution sharply decreases when the chromium content of the alloys increases. Transition from the region of the γ solid solution to the two-phase γ + α region is accompanied in all cases by a significant increase in the bending deflection. Consequently, for this quaternary system, as for the ternary system, Fe – Ni – Cr [1], it is confirmed that heterogenization of the γ solid solution by the second solid solution, α, leads to a reduction in the heat-stability of the alloys, or the resistance of the alloys to plastic deformation at high temperatures. Here it should be noted that there is no direct relationship between changes in strength at room temperature (as shown by hardness) of alloys with heterogeneous and homogeneous structures in their composition and the heat-strength of the same alloys. On the contrary, heterogeneous alloys possessing a high degree of hardness at room temperature show the lowest heat-strengths at 800° (see Figs. 3, 4, 5, and 6).

It is also of interest that, for the section of the iron – chromium – nickel – manganese quaternary system considered here, an increase in the bending deflection of the alloys becomes evident long before the composition enters the two-phase region. The increase is noticeable even before the composition reaches the boundary of the solubility limit of the components in the γ solid solution. Examination of the alloys, before application of the bending forces, by microanalysis and by measurement of specific electrical resistance and hardness, failed to reveal the presence of a two-phase system in any of those which had a composition in the γ solid solution region close to its boundary, and which showed a decrease in the bending deflection before this boundary is crossed. There is reason to believe that the increased plastic flow of the solid solution in this system, as shown by alloys of composition close to the solubility limit, is connected with the degree of tempering of the original solid solution and with other factors.

Our experiments show that manganese does not reduce the plastic deformation resistance of alloys having compositions corresponding to the solid solution of the iron – chromium – nickel – manganese quaternary system. On the contrary, an increase in manganese content leads to an increase in this resistance, though the effect is slight. This can be seen from Fig. 7, which shows the relationship between the bending deflection of alloys of the section under discussion and the manganese content, the chromium content being kept constant at 20%. The experimental points were obtained by testing for 11 hours at 800° and 4 hours at 900°. From the results given

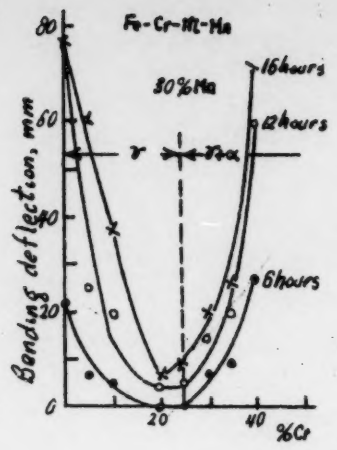

Fig. 6. Relation between bending deflection of quaternary alloys at 800° and chromium content (30% manganese).

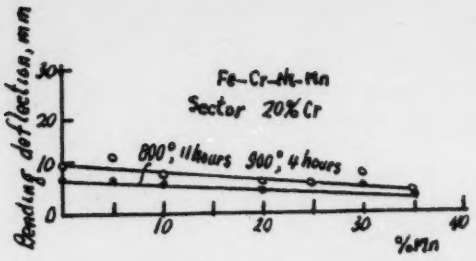

Fig. 7. Effect of manganese on the bending deflection at 800° on the quaternary γ solid solution.

here it may be concluded that for some alloys for use at high temperatures the nickel content can be reduced at the expense of the manganese. It should, however, be borne in mind that an increase in the manganese content leads to a reduction in the heat stability of the alloy. For this reason, when manganese is used in the preparation of alloys, other elements which increase the heat stability should also be included. As will be evident from the literature, other authors, studying manganese alloys by different methods, have arrived at similar conclusions.

SUMMARY

1. The results are given of a study of alloys of one section of the iron—chromium—nickel—manganese quaternary system, in which measurements were made of the electrical resistance and the hardness at room temperature, and of the heat-strength at 800°.

2. The composition—heat-strength diagram for the alloys of this system shows that in the region of the quaternary γ solid solution the heat-strength markedly increases with the chromium content of the solid solution. An increase in the chromium content above the saturation limit or into the region of the γ + α phases leads to a sharp reduction in the deformation resistance of the alloys at 800°.

3. The hardness of the heterogeneous alloys (γ + α phases) at room temperature sharply increases with an increase in the chromium content, but the heat-strength of the alloys in the same heterogeneous region is sharply reduced.

4. An increase in the manganese content of the quaternary solid solutions results in a slight increase in the heat-strength of these alloys.

From the experimental results obtained, it can be stated that in many alloys which have as their basis the system iron—chromium—nickel, a considerable quantity of the nickel can be replaced by manganese without materially altering the plastic deformation resistance. But this replacement of nickel by manganese should always be accompanied by the inclusion of supplementary alloying components which are capable of increasing the heat stability of the alloys.

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THERMOCHEMICAL INVESTIGATIONS OF SOLUTIONS

COMMUNICATION 5. VAPOR PRESSURE AND COMPOSITION OF THE BINARY SYSTEM $CH_3CHO + H_2O$

A. A. Dobrinskaya, V. G. Markovich, and M. B. Neiman

In the course of our work on the cold-flame oxidation of hydrocarbons [1-3], we found it necessary to distil aqueous solutions of various aldehydes, including acetaldehyde. It was found that there is practically no data in the literature on the vapor pressure and composition of acetaldehyde solutions. However, this problem is of theoretical as well as practical interest, since it is known that acetaldehyde tends to form hydrates, and for this reason its aqueous solutions should show large deviations from the laws of ideal solutions.

The vapor pressure and composition of aqueous solutions of acetaldehyde were determined by Pascal and his coworkers [4], by Kovalev [5], and by Bushmakin and Kuchinskaya [6]. The work of Pascal was carried out over 30 years ago by the method of distilling mixtures of acetic acid, acetaldehyde and water; it was intended to provide data required by chemical factories engaged in the production of synthetic acetic acid. Bushmakin and Kuchinskaya give total vapor pressures for dilute solutions only.

Tentative values for the partial vapor pressure of acetaldehyde were obtained by these authors on the assumption that the partial vapor pressure of the water could be calculated from Raoult's law. Such an assumption is, or course, open to criticism. Because of the faulty methods used by Kovalev in that part of his work dealing with the determination of vapor tension, his results cannot be regarded as trustworthy.

In view of this situation, we undertook the work of determining the vapor pressure and composition of aqueous acetaldehyde solutions over a wide range of concentrations and in the temperature interval 0 to 25°.

EXPERIMENTAL

1. Experimental methods

The acetaldehyde used was prepared from commercial acetaldehyde through paraldehyde, the paraldehyde being purified by double distillation. The acetaldehyde was obtained by depolymerizing the paraldehyde with the aid of a small quantity of concentrated sulfuric acid, and it was then twice distilled in a nitrogen atmosphere. The product has a boiling point of 19.8° at 760 mm; its vapor pressure values at different temperatures agreed closely with the values obtained by Gilmour [7].

The acetaldehyde content of the solutions was determined by the hydroxylamine method. As will be seen from the results of several analyses given in Table 1, acetaldehyde can be determined by this method with an error not exceeding 1-1.5%. The total vapor pressure of the acetaldehyde solutions was determined by the static method already described by one of the present authors, [8].

TABLE 1

Test of Hydroxylamine Method for Accuracy

Concentration of CH_3CHO, in weight %					CH_3CHO found, as% of taken
Taken	Found				
	I	II	III	Mean	
2.86	2.84	2.84	2.81	2.83	98.9
4.85	4.89	4.85	4.87	4.87	100.4
8.20	8.08	8.07	8.09	8.08	98.5
20.5	20.30	20.36	20.39	20.35	99.2

A vacuum apparatus, part of which is shown diagrammatically in Fig. 1, was set up for the preparation of air-free acetaldehyde solutions. The vessel 1, containing acetaldehyde, was connected to the vacuum line by means of a rubber tubing. The acetaldehyde was cooled in liquid air and the apparatus was evacuated through taps 2 and 5, with tap 7 open. The Dewar vessel of liquid air was then placed under vessel 3, tap 5 was closed, and the acetaldehyde was distilled into 3. The air which was given off in this process, and whose pressure could be measured by the manometer 8, was pumped out, tap 2 being closed and tap 5 open. Then tap 5 was closed, the Dewar vessel brought under 4, and the acetaldehyde was distilled 3 into 4. The air given off was again pumped out. The process of distilling the acetaldehyde from 3 into 4 and back again, the air being pumped out after each operation, was repeated until air was completely removed from the apparatus.

Taps 5 and 7 were next closed and the solidified aldehyde was retained in vessel 3 or 4. Vessel 11, containing distilled water, was then attached to the line by means of rubber tubing. The water was frozen, and the air pumped out through taps 12 and 10. Tap 10 was next closed, and the Dewar vessel of liquid air brought under 9, into which the water was distilled. The air liberated from solution was pumped out. Air was completely removed from the system by distilling the water backward and forward between vessels 11 and 9, the air being pumped out after each operation. The trap 6, cooled with liquid air, prevented both water and acetaldehyde from reaching the pump during all these operations.

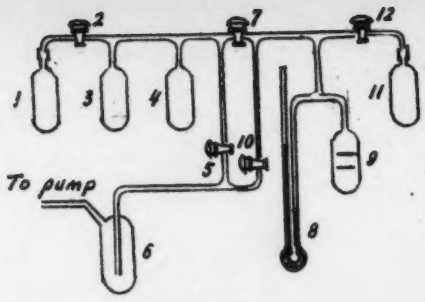

Fig. 1. Diagram of apparatus for the preparation of air-free solutions of acetaldehyde in water.

Two marks were made on vessel 9, the upper one corresponding to the total volume of solution to be prepared, and the lower one to the volume of the water component of this solution. A sufficient quantity of water was distilled into vessel 9 to bring its level a little above the mark. Tap 12 was then closed, and the excess water together with traces of air was pumped out through tap 10. Tap 10 was closed, and the water in 9 frozen. Tap 7 was opened and the acetaldehyde was carefully distilled into 9 until the level of the solution reached the upper mark. Tap 7 was then closed, and the vessel 9, together with the manometer, was sealed off from the apparatus at the neck. The solution was mixed by shaking the vessel. The vessel was then immersed in a thermostat, the temperature of which was maintained constant to within 0.01°. In order to avoid condensation of the vapors, the part of the apparatus which protruded from the thermostat was heated by means of an electric current. The vapor pressure of the solution was determined at 0, 12.04, and 24.77°. After the measurements had been made, the solution was frozen, the vessel opened, and the acetaldehyde content of the solution determined by the hydroxylamine method.

The partial vapor pressure of acetaldehyde was determined by a dyanmic method which has often been employed by Vrevsky [9,10], by Schawa and Butler [11], as well as by other workers. The apparatus is shown diagrammatically in Fig. 2. The method of operation of this apparatus is briefly described below.

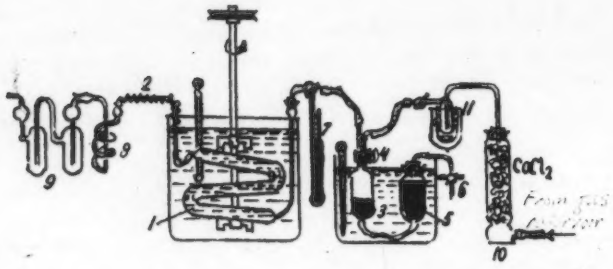

Fig. 2. Diagram of apparatus for the determination of the partial vapor pressure of acetaldehyde by the dynamic method.

The mercury gas reservoir 3, was filled to the mark with dry nitrogen, passed through the the tower 10 and the trap 11; its pressure was read on the manometer 7, and the temperature was also taken; tap 4 was then closed and the levelling vessel 5 raised. The bubbler 1 was filled with cooled acetaldehyde solution by means of a funnel connected to the inlet tube with a ground joint. The exit tube openings of the bubbler were closed with stoppers. The bubbler was placed in a thermostat heated a little above the required temperature and connected to the manometer, the three-way tap being in the closed position. The heater of the exit tube 2 was switched on. The trap 8, closed with stoppers, was weighed on an analytical balance. One end of it was then connected to the sulfuric-acid bubble-gage 9, after which it was immersed in liquid air contained in a Dewar flask. When the pressure in the trap had reached atmospheric, the gage was connected to it at the return end. When the thermostat had reached the required temperature, the exit tube of the bubbler was connected with the trap; the tap 4 was carefully opened and the bubbling of nitrogen commenced at the rate of 15-20 bubbles per 10 seconds, which corresponds to ~500 ml per hour. The time of commencement of the experiment was noted from here. In some experiments, carried out to check the nitrogen absorption, the higher flow rate of about 500 ml per hour was employed. A constant rate of flow was maintained by gradually raising the levelling vessel 5 and checking on the bubble-gage. When all the nitrogen from the gas reservoir had passed through, tap 4 was closed, the trap was cut off from the bubbler, the exit tube of which was stoppered. The time of ending the experiment was noted here. During the course of the experiment, records were kept of the temperature of both thermostats, and of the pressure and rate of flow of the gas. At the end of the experiment, the trap was removed from the Dewar vessel, and kept with one exit tube open until the contents began to melt so as to equalize the pressure; it was then completely stoppered to prevent acetaldehyde losses. When the trap had reached room temperature it was weighed, after which its contents were transferred to a volumetric flask; the solution was made up to the mark and samples analyzed.

The volume of acetaldehyde vapor was calculated from the formula

$$V_{CH_3CHO} = \frac{22400 \cdot T \cdot 760 \cdot x}{273 \cdot p \cdot 44}, \quad (1)$$

where T is the absolute temperature, x is the weight of acetaldehyde collected, and p is the pressure at which the experiment is carried out. The water vapor volume, V_{H_2O}, was calculated from a similar formula; the nitrogen volume V_{N_2}, was easily calculated from the volume of the mercury gas reservoir (447.7 ml) and the temperature and pressure of the nitrogen. The partial vapor pressure of acetaldehyde was calculated from the formula:

$$p_{CH_3CHO} = \frac{pV_{CH_3CHO}}{V_{N_2} + V_{CH_3CHO} + V_{H_2O}}. \quad (2)$$

2. Experimental results

First we determined the total vapor pressures of acetaldehyde solutions and calculated the partial vapor pressures of acetaldehyde by means of Duhem's formula [12]. In order to check the validity of these calculated values, we made experimental determinations of the partial vapor pressure of acetaldehyde on a number of solutions.

Determination of the vapor pressure of the binary system $CH_3CHO + H_2O$. The results of our experimental determinations of the total vapor pressures of aqueous acetaldehyde solutions by the static method are given in Table 2.

The values we obtained for the vapor pressure of pure acetaldehyde agree to within 3-5 mm with those given by Gilmour [7] and by Roth [13].

Our results may be expressed by the formula

$$\log p = 7.821 - \frac{6000}{2.3\ RT}, \quad (3)$$

from which it follows that the latent heat of vaporization of acetaldehyde in the temperature range 0-25° is equal to 6000 cal/mole. This value is in good agreement with the latent heat values found by Roth [13] (6020 cal/mole), and by Berthelot [14] (6000 cal/mole). In calculating the partial vapor pressures by Duhem's formula we attempted to make use of the method of Margules [15]. However, the use of this method with exponential terms containing only second and third powers of x gave unsatisfactory results. We therefore used the method of successive approximations proposed by Bose [16]. Using this method, we derived values for the partial vapor pressures of acetaldehyde and water from their sum

TABLE 2

Total Vapor Pressures of Aqueous Acetaldehyde Solutions

Quantity of acetaldehyde in solution		Pressure in mm Hg at temperature in °C		
Weight %	Mol. %	24.77	12.04	0.0
11.4	5.0	189.5	89	40
27.6	13.4	436	219	90
36.2	18.9	564	312	139
50.2	29.3	672	383	191.5
76.7	57.4	769	470	277
81.5	64.3	789	483	282
86.6	72.7	791	488	292
96.0	90.6	841	524	315
100.0	100.0	761*	562	346.5

* This determination was carried out at 19.8°.

$$p_{CH_3CHO} + p_{H_2O} = p \quad (4)$$

and the relationship

$$\frac{p_{CH_3CHO}}{p_{H_2O}} = -\frac{x}{1-x} \frac{\frac{dp_{CH_3CHO}}{dx}}{\frac{dp_{H_2O}}{dy}} \quad (5)$$

The latter relationship follows from Duhem's formula. Calculated partial vapor pressures of acetaldehyde for a number of solutions are given in Table 3. Total and partial vapor pressure curves of the solutions are shown in Figs. 3, 4, and 5. As will be seen from the curves, the vapor pressure of acetaldehyde solutions at all the temperatures studied have higher values than would be found if the solutions were ideal. The vapor pressure curves show no extreme values; therefore by Konovalov's law [17] aqueous solutions of acetaldehyde do not form azeotropes.

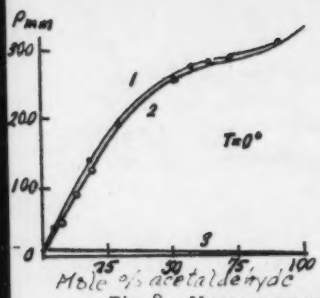

Fig. 3. Vapor pressure curves of the binary system $CH_3CHO + H_2O$ at 0°: 1) total vapor pressure; 2 and 3) partial vapor pressures of acetaldehyde and water.

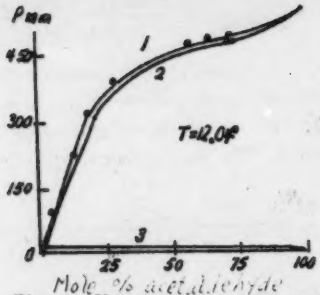

Fig. 4. Vapor pressure curves of the binary system $CH_3CHO + H_2O$ at 12.04°. 1) total vapor pressure; 2 and 3) partial vapor pressures of acetaldehyde and water.

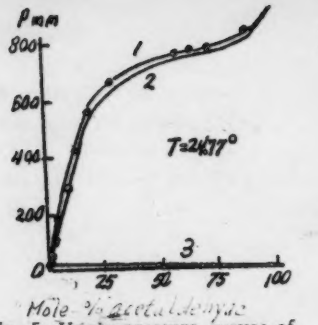

Fig. 5. Vapor pressure curves of the binary system $CH_3CHO + H_2O$ at 24.77°: 1) total vapor pressure; 2 and 3) partial vapor pressures of acetaldehyde and water.

Determination of the partial vapor pressures of acetaldehyde. Using the dynamic method, we determined the partial vapor pressures of acetaldehyde at 0 and at 24.77 The results of the experiments at 24 77 are given in Table 4.

As will be seen from a comparison of columns 3 and 4 in Table 4, where experimental results obtained in duplicate experiments on solutions containing 2 mole % CH_3CHO are given, good agreement is obtained in duplicate experiments. We carried out similar experiments at 0° on solutions containing 7.6, 13.0, 18.3, and 50.8 mole % of acetaldehyde. The results obtained are given in Table 5.

The difference between the results of duplicate experiments rarely exceeds 2%, even when concentrated acetaldehyde solutions having partial pressures as high as 350 mm are used.

Our experimental values for the partial vapor pressure of acetaldehyde are in good agreement with the corresponding values calculated from total vapor pressures by the Bose method. This is evident from an examination of Figures 3 and 5, where the experimental values denoted by circles closely follow the full line, which is drawn through the points obtained from the calculated values.

TABLE 3

Partial Vapor Pressures of Acetaldehyde Calculated by the Method of Bose

Quantity of acetaldehyde, mol. %	Pressure in mm Hg at temperature in °C		
	24.77	12.04	0.00
10	315	159	68
20	558	293	134
30	655	379	192
40	702	426	236
50	734	454	263
60	755	470	276
70	773	477	284
80	792	490	297
90	827	510	312

TABLE 4

Partial Vapor Pressure of Aqueous Acetaldehyde Solutions at 24.77 °C.

Concentration of acetaldehyde in solution	weight % / mole %	2.6 - 1.05	4.85 2.0	4.85 2.0	8.2 2.5	20.4 9.50
Experiment No.		2	3	4	6	8
Nitrogen passed, in ml		457.8	462.5	459.3	457.3	461.1
Total weight of condensate, in g		0.0662	0.1018	0.1022	0.1763	0.6473
Weight of acetaldehyde, by analysis, in g		0.0430	0.0817	0.0814	0.1530	0.6180
Weight of water, by difference, in g		0.0232	0.0201	0.0207	0.0233	0.0293
Volume of acetaldehyde vapor, in ml		23.5	45.1	45.0	83.6	337.5
Total volume of nitrogen and vapors, in ml		512.3	534.7	532.2	572.0	837.7
Pressure, in mm		772.5	766.0	766.2	773.5	774.7
Acetaldehyde vapor pressure, in mm		35.5	64.6	64.8	113.1	312.0

TABLE 5

Partial Vapor Pressure of Acetaldehyde over Its Aqueous Solutions at 0°

Quantity of CH_3CHO		Pressure, in mm Hg		
Weight %	Mole %	Expt. 1	Expt. 2	Expt. 3
33.6	7.6	55.2	54.0	54.6
50.3	13.0	90.2	90.8	90.5
63.1	18.3	129.1	129.0	129.1
71.5	50.8	353.3	348.7	351.0

DISCUSSION OF RESULTS

Our values for the vapor pressure and composition of aqueous acetaldehyde solutions may be used to calculate the approximate heats of formation of the solutions. Indeed, as Kirchhoff [18] has shown, the partial vapor pressure of one component of a solution increases with temperature according to the law

$$\frac{d \ln p_1}{dT} = \frac{\lambda_1 + \frac{dQ_1}{dx}}{RT^2} . \qquad (6)$$

Here λ_1 is the latent heat of formation for the vapor of this component, and (dQ_1/dx) is its differential heat of solution. From a knowledge of λ_1 and the value of $\underline{p}$ for solutions of different concentration at a number of temperatures, the value of (dQ_1/dx) may be calculated for a series of solutions. Then, by the method of graphic integration, $Q_1 = \underline{f}(x)$ may easily be found, and $Q_2 = F(x)$ and (dQ_2/dx) may be obtained by fairly simple calculations.

In carrying out this calculation, we plotted our values for the partial vapor pressure of acetaldehyde in the form of log $\underline{p}$ against $(1000/T)$ for a series of solutions (Fig. 6). Since the latent heat of vapor formation $\lambda_{CH_3CHO} = 6000$ cal/mole, values of (dQ_1/dx) for the different solutions may easily be obtained from the slopes of the lines in Fig. 6. It is clear from Fig. 6 that the value (dQ_1/dx) increases regularly as the concentration of the acetaldehyde solutions decreases. Having found the heat of solution $Q = \underline{f}(x)$ by graphic integration, we calculated the heats of formation of the solutions

$$CH_3CHO + xH_2O \quad (Q_2)$$

$$H_2O + xCH_3CHO \quad (Q_1)$$

The curves $Q_1 = \underline{f}(x)$ and $Q_2 = F(x)$ calculated in this manner are shown in Fig. 7.

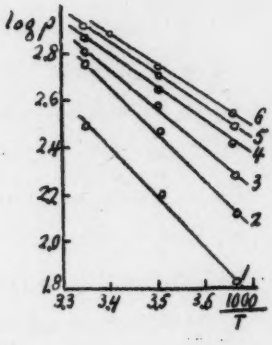

Fig. 6. Relation between partial vapor pressure of acetaldehyde and temperature. The straight lines 1,2,3,4,5 and 6 refer to aqueous solutions containing 10, 20, 30 50, 90, and 100 mole % of acetaldehyde.

As a check on the calculations, the formula giving the relationship between the temperature and total vapor pressure of binary solutions may be used:

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \qquad (7)$$

According to Vrevsky [19]

$$L = x'\lambda_1 + (1-x')\lambda_2 + x' \frac{dQ_1}{dx} + (1-x') \frac{dQ_2}{dx} \qquad (8),$$

where x' is the mole fraction for vapor; λ_1 and λ_2 are the latent heats of evaporation, and (dQ_1/dx) and (dQ_2/dx) are the differential heats of solution of the components.

TABLE 6

Comparison of Calculated and Experimental Heats of Formation

Composition of solution, %	Composition of vapor, x'	$\frac{dQ_1}{dx}$	$\frac{dQ_2}{dx}$	$L_{calc.}$ (cal/mole)	$L_{Expt.}$ (cal/mole)
10	0.94	3900	400	9950	10100
20	0.97	3000	800	9050	8950
30	0.975	1900	1200	7980	8050
50	0.98	600	2000	6700	6600
90	0.99	100	3000	6200	6270

The results calculated by means of this formula are compared in Table 6 with the $L_{Expt.}$ values, determined experimentally.

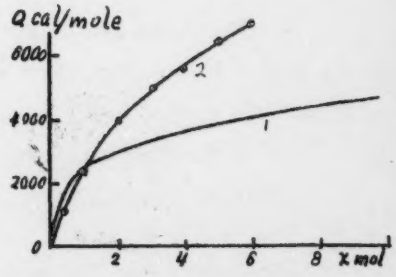

Fig. 7. Heat of solution curves for aqueous acetaldehyde solutions. 1) $H_2O + xCH_3CHO$; 2) $CH_3CHO + xH_2O$.

As will be seen from Table 6, the values of $L_{Expt.}$ and $L_{Calc.}$ do not differ by more than 1.5 %.

Unfortunately, we are not aware of any work on the determination of the heat of formation of acetaldehyde solutions; it was therefore not possible to compare our values calculated from vapor pressure measurements with values determined calorimetrically.

SUMMARY

1. The vapor pressures of a series of aqueous acetaldehyde solutions have been determined by a static method within the temperature range 0 to 25°.

2. The composition of the vapor of a series of aqueous acetaldehyde solutions has been determined by a dynamic method.

3. The method of Bose has been used to calculate the partial vapor pressures of acetaldehyde and water for solutions of $CH_3CHO + H_2O$ at various temperatures.

4. Heats of formation of aqueous acetaldehyde solutions have been calculated from vapor pressure measurements.

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ELECTRON MICROSCOPIC INVESTIGATION OF CHANGES IN THE SURFACE OF SOLID CATALYSTS DURING OPERATION

A. B. Shekhter and I. I. Tretyakov

In catalysis several factors are known which point to the extensive change in solid contacts during operation. The most striking of these is the well-known disintegration or, after long operation, complete destruction of platinum gauze in the oxidation of ammonia under industrial conditions; the roughening of the smooth surface of copper during the decomposition of ammonia [1] has also been described. The ordinary microscope when used for the investigation of these phenomena did not make it possible to study small submicroscopic changes taking place on the surface of the operating catalysts, and did not permit any further development in the concept of the disintegration of the smooth surface in operation. In addition, this method only allowed changes which had already taken place to be recorded.

The development of modern electron microscopy with its high resolving power prompted us to utilize this method for the detailed study of the structure of catalyst surfaces in operation.

As is known, for an electron microscopic investigation of the surface of solid objects, use must be made of the well-known replica method, i.e., the making of very fine molds which accurately reproduce the relief of the surface studied*. We used colloidal replicas, shading for greater contrast by means of a molecular stream of chromium directed at an acute angle on the surface of the replica**.

The suitability of this method for the study of metallic catalyst surfaces and the entire agreement between the electron microphotographs of the replicas with the relief of the surfaces producing them has been shown already for a number of examples [2]. By the use of the electron microscope method, it has been shown that the surface of fresh palladium sheet is comparatively smooth, and has only slight irregularities before use, but after a long time in use, large protuberances in the form of crystal formations of different sizes are seen [2]. In these samples the extreme surface heterogeneity was striking; each field of view in the electron microscope was noted for its structural characteristics, and it was impossible to discern any order in the distribution of the randomly distributed crystals. These photographs permitted it to be established without doubt only that there was a general tendency for catalysts to change in operation, and especially to form crystalline formations on a previously smooth surface.

It was shown by special experiments that changes in the surface of palladium and platinum similar to those which occur in the catalytic reaction are not produced by the action of the components of the reaction mixture (oxygen and hydrogen) on the reaction product (water vapor) at the reaction temperature, or by heating the catalyst in vacuum to the same temperature. This is well shown on a large number of electron microscope and ordinary microscope photographs, from which, because of lack of space, we only give one example illustrating the effect of heating a polished palladium plate in vacuum at 600° (see Fig. 2). From the photograph it is evident that, although the sample surface shows boundaries between crystalline granules characteristic of the metal recrystallization processes, the polished marks on the surfaces are fully retained, and there are no traces of disintegration of the surface.

It may be considered as established that the disintegration of catalyst surfaces is definitely connected with the catalytic reaction itself.

EXPERIMENTAL

For a detailed study of the early stages of the gradual disintegration of the operating surface of palladium and platinum, further experiments were carried out on the process of hydrogen oxidation on polished sheets of metal. The sheets were polished on a shammy disk, using chromium oxide; after polishing, the metal surface acquired a characteristic and easily reproducible form which facilitated the observation of small changes

* The degree of accuracy of reproduction of the replica of small relief details of the surface depends on the type of replica employed; in our case the accuracy was approximately 100 A.

** As a result of "shading", the protuberances on the replica surface reflect a shadow, as the chromium is prevented from falling on the corresponding areas of the surface. Moreover, on those parts of the surface which form different angles with the molecular stream, films of chromium having different thicknesses are formed, and in the microphotograph they show various degrees of blackening.

TABLE

Catalyst Temperature at Various Reaction Velocities

Catalyst	Nitrogen in mixture, percent	Total rate of mixture stream, liters per hour*	Catalyst temperature, °C	Duration of expt., in hours	Disintegration of catalyst surface
Palladium	85	1.2	250	40	None
	70	1.5	350	19	"
	43	2.3	450	3	Considerable
Platinum	25	4	600	5	"
	20	5	650	3	"

*The velocity of the nitrogen stream in all experiments was one liter per hour

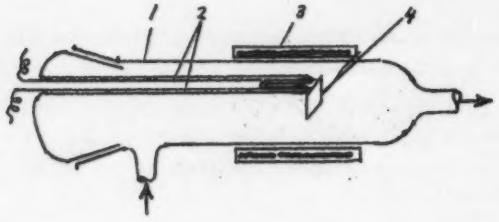

Fig. 1. Diagram of reaction apparatus.

in the surface structure of the catalysts*.

The oxidation of hydrogen on platinum and palladium was carried out in the apparatus shown in Fig. 1. A measured stream of explosion mixture diluted with nitrogen was passed through the reactor 1. The catalyst, in the form of metallic sheets 4, 4.5 by 9 mm and 0.3 mm thick connected to a platinum-platinum-rhodium thermocouple sealed in glass, was placed in the reactor perpendicular to the gas stream. The reactor was surrounded by the furnace 3, the temperature of which was kept constant and uniform at 160° in all experiments by means of a thermoregulator.

The rate of the catalytic reaction was varied by changing the velocities of the gas stream and the degree of dilution by nitrogen of the stoichiometric mixture of hydrogen and oxygen. The rate of the mixture stream changed within the range of 1.2 to 5 liters per hour, and the nitrogen content in this mixture from 20-85%.

Because of the exothermic hydrogen-oxidation reaction, the temperature of the metallic catalyst was higher than the temperature of the surrounding furnace (160°), and rapidly increased with an increase in the reaction rate (see Table).

By the selection of suitable mixtures and velocities, it was possible to find experimental conditions under which heating, as shown above, did not cause material changes in the surface, but the catalyst reaction itself produced sufficiently rapid characteristic rearrangements of the catalyst surface. Table 1 shows that these conditions were observed: for 43% nitrogen in the mixture, a total stream velocity of 2.3 liters per hour for palladium; and with 24% nitrogen in the mixture, a stream velocity of 4 liters per hour for platinum. Several series of experiments were carried out under these conditions to study the gradual disintegration of polished palladium and platinum.

The catalysts, after they had been working for a definite time interval, were removed from the reaction apparatus and replicas were made from them, after which they were replaced for further operation; as has been shown above, the contact activity did not noticeably change when a colloidal replica was made. The series of experiments showed mainly that the surface of the operating catalyst loses abrasions — traces due to polishing. This is illustrated by the photograph of polished palladium after three hours working (Fig. 3). Furthermore, the main part of the smooth catalyst surface became wavy (Fig. 4, photograph of platinum after 5 hours); then, after further work, the wavy surfaces acquired an angular character, and gradually formed a step-like crystalline structure [see photograph of platinum after 10 hours (Fig. 5) and after 15 hours (Fig. 6), and palladium after 20 hours (Fig. 7)].

We note that on the polished surfaces, which were apparently homogeneous up to the time of working, a sharp heterogeneity in the surface disintegration was observed after operation. As well as a more or less large disintegrated area of the surface, completely smooth areas were also encountered. In Figs. 8, 9, 10, 11, and 12, several of the different types of surface disintegration observed are shown. As a rule, the areas characterized

*In order to remove aberrations in the metal structure arising from previous mechanical treatment, the samples were tempered before being polished by heating for a few minutes to 1200° in the case of platinum, and to 800° in the case of palladium.

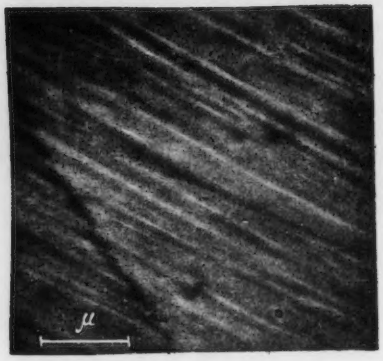

Fig. 2. Polished palladium sheet heated in vacuum at 600°. X 16,000.

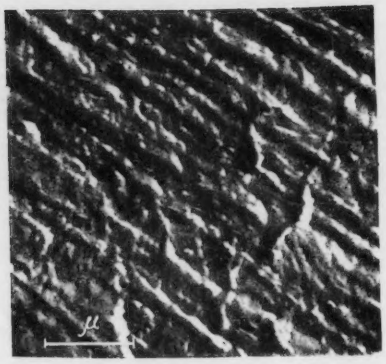

Fig. 3. Polished palladium catalyst after 3 hours in operation. X 16,000.

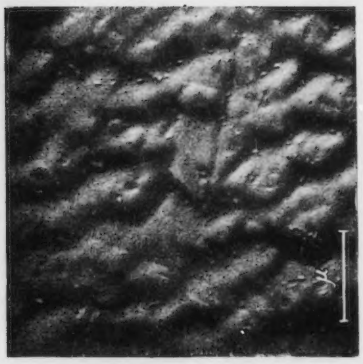

Fig. 4. Polished platinum catalyst after 5 hours in operation. X 16,000

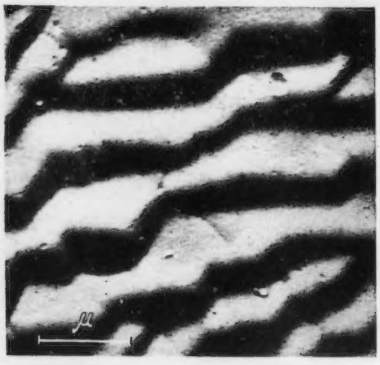

Fig. 5. The same catalyst after 10 hours. X 16000.

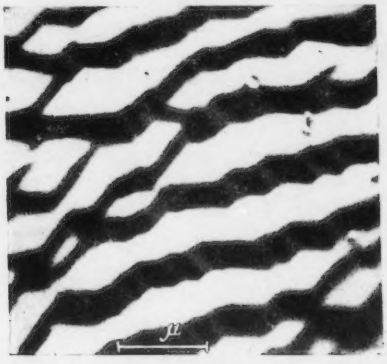

Fig. 6. The same catalyst after 15 hours. X 16,000.

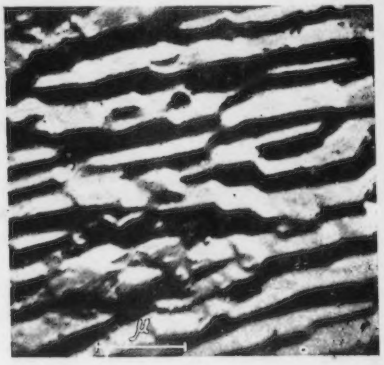

Fig. 7. Polished palladium catalyst after 20 hours in operation X 16,000.

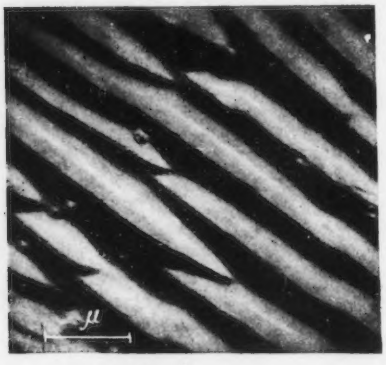

Fig. 8

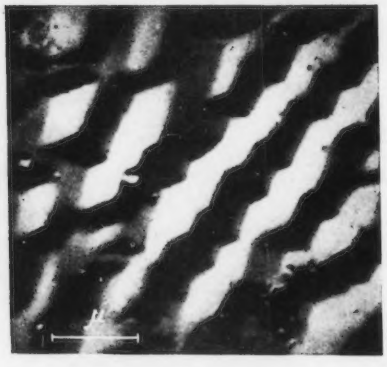

Fig. 9

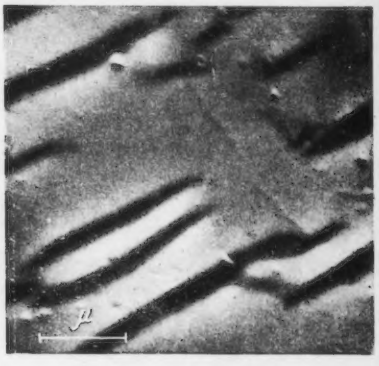

Fig. 10

Fig. 8, 9, 10, 11, 12 (11 and 12 are on the following page): Different parts of a platinum catalyst after 15 hours in operation. X 16,000.

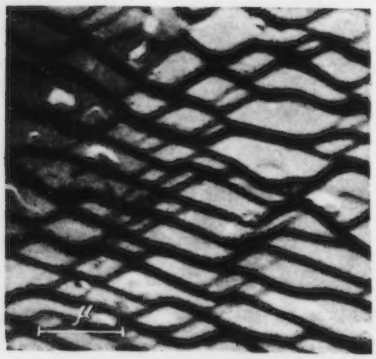

Fig. 11. Caption on previous page.

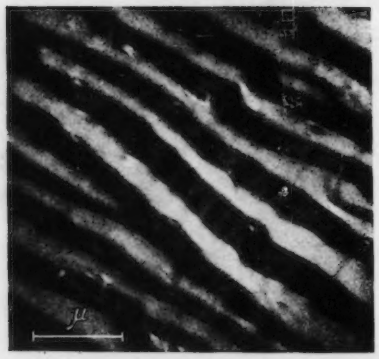

Fig. 12. Caption on previous page.

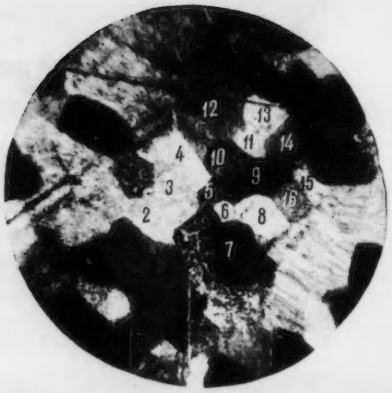

Fig. 13. Visual photograph of platinum catalyst after 15 hours in operation X 170.

Fig. 14. Boundaries between different zones on an operating palladium catalyst. X 16,000.

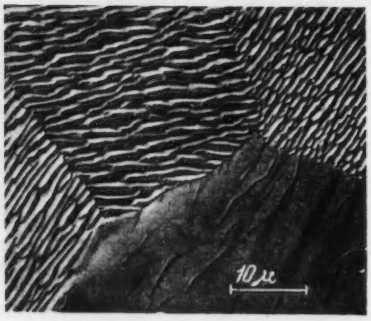

Fig. 15a. Different disintegration zones on a platinum catalyst after 150 hours in operation.

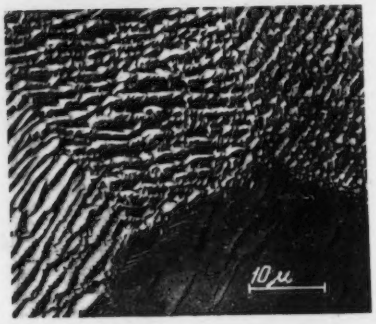

Fig. 15b. The same zones after 440 hours of catalyst operation.

Fig. 16. Part of zone No. 8 on platinum catalyst after 15 hours in operation. X 16,000

Fig. 17. Visual microphotograph of platinum-rhodium catalyst after 82 hours in operation at 600° X 310.

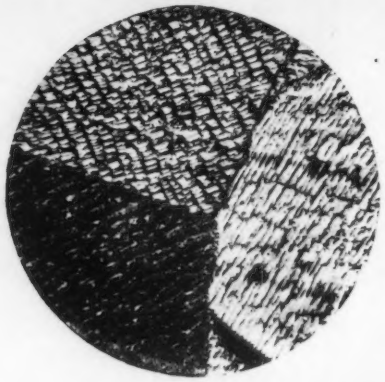

Fig. 18. Visual microphotograph of copper catalyst after 30 hours in operation at 470° X 310.

by one or the other type of disintegration, are too large to be placed on the field of view of the electron microscope ($\sim$0.01 mm^2), and for this reason their distribution on the catalyst surface was studied on a visual microphotograph with magnification of $\sim$200. In the microphotographs obtained in this way, it is seen that the surface of the working catalyst has well-bounded zones possessing irregular polygonal features. The nature of the surface disintegration inside each "zone" is the same for all the "zones" but individual "zones" differ considerably in the characteristics of their surface structure [3].

Figure 13 shows a visual photomicrograph (magnification 170) of a polished platinum plate after 15 hours operation in explosion mixture, diluted with 25% of nitrogen, at 600°. On this, individual marked "zones" are visible, and in spite of the small magnification it is possible to note differences in the nature of the disintegration in different "zones". The picture seen directly in the visual microscope looks more effective than the photograph, because different "zones" showed different colorings (blue, light blue, orange, green, brown, and other tints). The "zone" size varied from about 0.01-0.2 mm in cross section. It is obvious, therefore, that in the electron microscope, in which the magnification is 10,000 and the field of view equal to 5 X 5 μ^2, it is impossible to see more than one "zone" entirely, and either a small part of a "zone" or the boundary between two neighboring "zones" with the adjoining regions is observed (for example, Fig. 14, photograph of the boundary between two "zones" on the surface of a platinum catalyst after operation).

In order to follow the gradual changes in individual zones with the aid of the electron microscope, it would be necessary to be able to take repeated photographs of replicas of the same submicroscopic areas. This problem is very difficult if the usual methods of making replicas are employed, and therefore the development of a special technique was necessary [4].

By the use of this technique, which allowed the repeated taking of replicas of given submicroscopic regions, it was possible to follow the successive stages in the disintegration of individual "zones"; for example, photographs in Figs. 4, 5, and 6 were made from the same zone denoted by the number 4 in Fig. 13, after the platinum catalyst had been working for 5, 10, and 15 hours. It was also possible to compose an electron microscope picture of the deposition of individual "zones" on the surface area examined.

Fig. 15 shows a small part of this electron microscope picture of a platinum surface after 15 hours (Fig. 15 a) and after 440 hours of working (Fig. 15 b). These photographs were taken with a magnification of 2000, and partly embrace 4 "zones". Although 3 "zones" in this surface acquired a marked crystalline character, one of these remained comparatively smooth after 440 hours.

The surface disintegration of platinum catalysts was followed in stages over a long period; it was thus shown that after 1000 hours working, the surface continues to disintegrate under the influence of a chemical reaction. It is of interest that several "zones" comparatively distant from one another, show extraordinarily similar structures (see, for example, in Figs. 6 and 16, the electron microphotographs of "zones" denoted No. 4 and No. 8 in the visual microphotograph Fig. 13). This gives rise to the impression that different "zones" disintegrate in different ways, but that the number of types of disintegration is fairly limited.

As visual microphotographs of platinum and palladium sheets after use show, their appearance in the visual microscope is very similar to the appearance of the same sheets after etching [3]. In both cases, the polishing marks (abrasions) disappear and individual areas or "zones" bounded from one another make their appearance.

It seems probable that the zones appearing on the metal surface in both cases are due to the same cause; in other words, the catalytic reaction exposes the crystalline structure of the metal in the same way as etching, and "zones" appearing correspond to the boundaries of the individual crystals making up the platinum surface.

The following experiment may be considered as confirmation of this idea. A polished palladium sheet was first etched with nitric acid and then used as a catalyst in the oxidation of hydrogen. After 10 hours, it was found that the zone boundaries (different in character from the disintegrated surface) accurately corresponded to the boundaries between the crystals which had appeared on etching [3]. The changes in the catalyst surface under the influence of the catalytic reaction described above suggest an extensive rearrangement in this surface, which can only be brought about if it is assumed that there is an intensive lateral movement of the catalyst surface atoms.

Experiments in which palladium and platinum were heated in vacuum in the individual components of the reaction mixture (to 1000°), showed that the cause of this increased lateral movement was not the increase in temperature which took place in our experiments. (Up to 450° in the case of platinum and up to 600° in the case of palladium). Consequently, the cause of this movement must be different and must be connected with the catalytic reaction itself; so, for example, the appearance of energy necessary to increase lateral movement may be connected with the action of active intermediate products formed in the reaction or with the formation

of unstable catalytic compounds which leave the lattice of the metal on the surface layer in a disturbed condition on decomposition.

Differences in the disintegration of individual "zones" under the action of the catalytic reaction are striking. This leads to the idea that different zones (evidently representing different boundaries of the crystal surface) have different catalytic activities. Thus, the experimental work given above may be of interest in connection with one of the most important problems of catalysis theory, the problem of the distribution of active centers on the catalyst surface; however, this picture may also be obtained as a result of differences in the stability of the different crystal boundaries which make up the surface toward disintegration.

The choice between these two explanations can only be made, evidently, on the basis of results of catalytic activity measurements on individual boundaries of a sufficiently large mono-crystal. In this connection, we have undertaken a study of the catalytic activity of the boundaries of mono-crystals.

Experiments on the oxidation of hydrogen at 430° on the individual boundaries of a specially-grown large copper monocrystal in a gas stream containing 98.5 % hydrogen and 1.5% oxygen showed that the reaction yield (per unit of surface) was approximately the same for boundaries (100), (110), and (111), while for boundaries (100) and (110)the reaction developed in a different manner and for boundary (111) it remained smooth during the course of the whole experiment (23 hours). This evidently points to the fact that there is no unambiguous correlation between the disintegration of surfaces and their catalytic activity.*

The disintegration of solid catalysts during reaction is not limited to the examples given above, but is apparently a more general effect which applies to a wide range of catalysts and processes, and to these belong a number of systems in which the changes have not been known up to now. When hydrogen is oxidized on solid copper and ammonia on platinum or platinum-rhodium alloys, we succeeded, with the aid of the electron microscopic methods, in observing extensive disintegration of the surface similar to that described above for platinum and palladium in the oxidation of hydrogen. With platinum-rhodium alloys the disintegration depends on the percentage of rhodium in the alloy.

This disintegration, which is shown by the appearance of crystal structures on the initial smooth catalyst surface, has also a zonal character (Fig. 17 — platinum-rhodium catalyst after operation and Fig. 18 — copper catalyst after operation; both photographs were made with a magnification of 310). Changes in the structure of the smooth surface of iron catalysts in the decomposition of ammonia were also observed.

SUMMARY

1. The data given in this paper show that the changes in solid metallic catalysts during operation are of much wider occurrence than has generally been considered up to now.

The metallic catalysts (Pt, Pd, Cu, Fe, alloys of platinum and rhodium) undergo characteristic and fairly complex changes in surface structure from the very beginning of operation, and these changes continue even during long periods of operation.

2. When catalytic reactions are carried out on tempered, polished, solid metallic catalysts, the electron-microscope method enables qualitative differences in the disintegration of the individual crystal boundaries which go to make up the polycrystalline surface to be observed ("zonality" of disintegration).

3. A parallel study of the disintegration and catalytic activity of the individual boundaries of a copper monocrystal in the oxidation of hydrogen showed that there is no well-defined functional relationship between the degree of disintegration in this reaction and the catalytic activity. Thus, it is impossible to draw conclusions about the catalytic activity of these surfaces from the differences in the disintegration of the boundaries in the reaction.

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* In the same way, it is possible to interpret the experimental results of Leidheiser and Gwathmey [5], who studied the oxidation of hydrogen at the boundaries (100) and (111) of a copper monocrystal under somewhat different kinetic conditions; they observed a higher catalytic activity at the undisintegrated boundary (111).

PROBLEMS OF THE CHEMISTRY AND TECHNOLOGY OF MINERAL FERTILIZERS IN CENTRAL ASIA*

S. I. Volfkovich

Progress in chemistry and biology and the deep interpenetration of these sciences is having an increasing effect on crop productivity. In recent years considerable successes have been achieved in the study of the nutrition cycle of elements, the assimilation and metabolism in plants, and in elucidating the functions of microorganisms and microelements. Our knowledge of functions of organic substances has been extended. Growth stimulators and growth suppressors have been discovered, synthesized, and introduced into practice. Some of these have been used to counter weeds (herbicides) and plant diseases (fungicides).

Many new and important developments in this borderland region between chemistry and biology have been introduced by Soviet scientists and agriculturists. Naturally, all this work, which is directed toward the achievement of an abundance of food products and industrial raw materials, makes a direct contribution to the building of Communism.

The further development of the chemistry, technology, and agricultural chemistry of fertilizers is of especially great significance in the republics of Central Asia, where the agricultural industries, using the products of the chemical industry on the basis of the achievements of Soviet agriculture, biology, and technique, have already made considerable progress. In his Report to the 19th Party Congress, Comrade Malenkov, mentioning the especially rapid rate of growth in the production of cotton and of sugar-beet in the post-war period, gave a highly authoritative appraisal of this progress. Comrade Beriya in his speeches to the 19th Party Congress, pointing out the achievement of the Soviet Eastern Republics in producing a harvest on the average of 21 centners of raw cotton per hectare, said: " In no cotton-producing country in the world is such a yield achieved as is reached by Soviet cotton pods. In 1951 the productivity of cotton in Egypt was 11.5 centners per hectare, in the United States 8.3, in India 3.4, in Pakistan 5.2, in Turkey 7.2, and in Iran 4.5 centners per hectare. It should be taken into account that the high yield of cotton in the Soviet Eastern Republics is obtained over large areas, which is borne out by the fact that the Soviet Republics mentioned produce as much cotton as India, Egypt, Iran, Turkey, and Afghanistan taken together" **.

The agricultural industry of the Central Asian Republics is noted for its extensive utilization of chemistry, for its high standards in the use of fertilizers for cotton, and for its high efficiency. There have been years in which fertilizers have been applied in insufficient quantities and in unsuitable forms, or with disproportionate relationships of nutritive elements, without considering the type of soil or manner of cultivation. In these years productivity was considerably reduced.

These circumstances make it necessary for chemists and agricultural chemists to consider the urgent problems arising in the further planned and purposeful study of the optimum conditions for the application of fertilizers in central Asia, and also the most suitable conditions for production of these fertilizers, taking into account the local conditions and sources of supply.

The 19th Congress of the Communist Party of the Soviet Union in its directives on the Five-Year Plan stipulated that in1955 the value of the production of raw cotton should be increased 55 to 65% in comparison with 1950. In the districts of Central Asia and Southern Kazakhstan the cotton harvest is to be increased to 26 to 27 cent centners per hectare.*** In the section devoted to the development of the chemical industry, the Directives of the 19th Party Congress called for a greater rate of increase in the production of mineral fertilizers.

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* Paper read at a combined session of the Division of Chemistry of the Academy of Sciences, USSR, and the Academy of Sciences of the Uzbek SSR, October 24, 1952, Tashkent.

** Address of L. Beriya at the 19th Congress of the All-Union Communist Party (Bolsheviks), State Political Press, 1952, page 16.

*** See Directives of the 19th Party Congress on the 5th Five-Year Plan for the Development of the USSR in 1951-1955. Pravda Press, Moscow, 1952.

For Central Asian irrigated agricultural land, the mineral fertilizers which are of the greatest importance are nitrogen and phosphorus fertilizers. These are the most effective. Potassium fertilizers are considerably less effective since most of the soil in Central Asia (gray desert soil) contains sufficient quantities of potassium, easily accessible for the plants. Potassium manuring is satisfactory only on meadow soils rich in organic substances and poor in lime, and then with liberal applications of nitrogen. Lime fertilizing is ineffective on the alkaline soils of Central Asia. Gypsum may acquire considerable importance as a chemical treatment for the saline soils which are encountered in various districts. In recent years field experiments by Soviet research institutes have established the effectiveness applying boron and manganese micro-fertilizers to cotton and alfalfa plants.

It is generally considered that the application of mineral fertilizers should be accompanied by the application of orgnaic fertilizers, of which cottonseed meal, dung, and in some districts peat are the most widely distributed and the most effective in Central Asia, both alone and as mixtures with mineral fertilizers. According to the data obtained in field experiments by the Central Asian Institutes and Geographical Stations of the Scientific Research Institute for Fertilizers and Insecticides (NIUIF), the approximate requirements per ton of nutritive element are: for the cotton plant, 1 ton of nitrogen per 12 to 14 tons of raw cotton, and 1 ton of P_2O_5 per 6 to 7 tons of raw cotton; and for alfalfa, 1 ton of P_2O_5 per 20 to 30 tons of hay.

The amount of fertilizers to be applied per hectare of sown area and the proportion of the nutritive elements in the fertilizer for the basic Central Asian cotton crop are different for different soils and conditions of cultivation.

Conventionally, for calculating the manure requirements in Central Asia, some technical-economics papers take the following averages: for cotton 100 to 110 kg nitrogen per hectare, 75 kg P_2O_5 per hectare, and 25 kg of K_2O per hectare; and for alfalfa, 76 kg P_2O_5 per hectare, and 25 kg K_2O per hectare. For complex and mixed fertilizers, agrochemists recommend a basic pre-seed fertilizer of approximately the following composition: $N:P_2O_5$ = 1:1; 1:2; and 1:3; and as a supplement with predominant nitrogen, approximately 2:1 and 1.5:1*.

The presence in the Central Asian Republics of large deposits of phosphates, sulfur, sulfide minerals, and potassium, and other salts, as well as water power and fuel resources, together with the large demand for fertilizers of high efficiency raises chemical problems, both pure and applied, the solution of which should ensure further developments in the production of mineral fertilizers and the utilization of chemicals in agriculture.

A little more than 25 years ago (in 1926) in Southern Kazakhstan in the ancient deposits of the Middle Cambrian growth of the Kara-Tau mountain range, Soviet geologists discovered large deposits of phosphorites of the blanket type [1], which were unknown up to that time in our country. In size of the blankets, their productivity, and extent of reserves, these phosphorite deposits are superior to any hitherto found in our country, being inferior only to Khibinsk apatites. However, they have the great advantage over these that they occur close to the important fertilizer-consuming districts of Central Asia. A disadvantage of the Kara-Tau phosphorites is their considerable variation in the content of phosphorus, silicon, magnesium, and other components from blanket to blanket, and in their comparatively high magnesium content, which affects the sulfuric acid treatment in the manufacture of superphosphates and concentrated phosphoric acid.

The finely dispersed structure and close growth of the minerals greatly hampers the mechanical and flotation enrichment of these phosphorites. Being metamorphosed apatites, the Kara-Tau phosphorites, as distinct from other organogenic phosphorites, cannot be used as direct fertilizers, especially on alkaline soils. Superphosphate prepared from the lower grades of these phosphorites is hygroscopic, and under unfavorable climatic conditions, forms cakes. The concentration of phosphoric acid obtained from these phosphorites is also difficult because of the separation of salt precipitates.

In recent years in the NIUIF, the Kazakh Academy of Sciences, and other scientific institutes, practically all the possible methods for the chemical conversion of the Kara-Tau phosphorites into fertilizers have been studied. Detailed studies have been made of the mineralogical and petrological composition, the structure and physical properties of these phosphorites, with the aid of crystal optical analysis, thermography, X-ray, and electron microscopy; several systems have been studied connected with the chemical decomposition of these phosphorites.

As a result of numerous investigations and pilot plant experiments, it may at present be considered established that the best methods for the chemical treatment of these phosphorites are the following:

1) The production of concentrated fertilizers—precipitated dicalcium phosphate, ammofos (a mixture of di- and mono ammonium phosphates), etc.

2) The production of ammoniated superphosphate by neutralizing the free acid with ammonia or ammon-

* Further experimental work should be done to determine exactly the optimum proportions of the nutrient elements.

ium salts (solution of nitrate of ammonia or other nitrogen-containing salts of ammonia).

3) The production of citrate-soluble phosphates by non-acid (thermal and alkali) processes: of meta- and pyrophosphates, fused and alkaline phosphates, etc.

The fertilizers enumerated may be obtained by various chemical processes. In the present short report it will be useful to consider only those processes in which phosphorites are treated with sulfuric acid, since these processes are the most widely used and are the predominant ones in our chemical industry. They include the production of superphosphate, phosphoric acid, and the concentrated fertilizers enumerated under (1) above. At the present time, as a sulfur-containing raw material there may be utilized sulfur, sulfides, sulfurous gases from nonferrous metallurgy, gypsum, alunite, and others. It is possible to regenerate sulfuric acid in the production of concentrated fertilizers as a result of the thermal decomposition of phospho-gypsum, with the production of sulfurous gases and cement.

The fundamental task of our superphosphate industry is the raising of the quality and especially of the physical properties of superphosphate obtained from the Kara-Tau phosphorites by concentrating the raw material, granulation [2], or ammoniation of superphosphate by ammonia. When superphosphate is ammoniated by means of ammonium salts, for example liquid ammonia and ammonium nitrate, phosphorus-nitrogen fertilizers with proportions of nutrient elements close to that required for basic pre-seed applications may be obtained.

It is sometimes thought that the application of concentrated fertilizers containing 2, 3, or 4 times more nutrient substances than the ordinary low-percentage fertilizers, such as superphosphate, ammonium sulfate, and others, is only an urgent production task for the most remote regions, such as the Kola Peninsula, from which apatite is transported to the Ukraine, the Caucasus, and to Central Asia. This results in an economy of milliards of ton-kilometers. However, this problem is also of great importance for the Central Asian Republics, because the distance from the Kara-Tau phosphorite deposits to many regions which consume fertilizers varies from a few hundred to fifteen hundred kilometers. Moreover, the use of concentrated fertilizers results in a saving in freight transportation, in work of applying the fertilizer to the soil, and also in packing and storage. All these taken together are very important, as is shown by economic calculations, under Central Asian conditions. Therefore, in the near future it will be advantageous to construct factories for the manufacture of concentrated fertilizers – ammofos, precipitated dicalcium phosphate, etc., in the Central Asian Republics.

The most concentrated and the most rapidly acting fertilizer which is of considerable interest in the fertilizing of the cotton plant (especially as a supplement) is ammofos, which contains about 50% P_2O_5 and about 14% nitrogen. This fertilizer, according to the results of Chumanov's experiments [3], is highly effective on gray desert soils, thanks to the mobility of this form of nitrogen-phosphate fertilizer in soils when it is applied at the time of vegetation (supplement). Moreover, the production of ammofos from the Kara-Tau phosphorites is one of the most efficient methods of working these phosphorites. The technology of the production of ammofos from apatite concentrates on an industrial scale has been mastered in our country.

As far as precipitated dicalcium phosphate is concerned, its preparation, from the economic point of view, is most efficiently carried out by the nitric acid or the hydrochloric acid decomposition of phosphate. The hydrochloric acid treatment of phosphates is efficient when effluent or very cheap hydrochloric acid is available. This gives calcium chloride as a by-product, which is troublesome and difficult to use [4]. Methods of utilizing it with the possible reversible production of hydrochloric acid have been proposed.

The decomposition of phosphates by nitric acid with the subsequent preparation of precipitated dicalcium phosphate and potassium and ammonium nitrates [5] seems to be one of the most promising for Central Asian technological conditions. These processes are based on the following main reactions:

$$Ca_5F(PO_4)_3 + 10\,HNO_3 = 3H_3PO_4 + 5Ca(NO_3)_2 + HF \qquad (1)$$

$$H_3PO_4 + Ca(NO_3)_2 + CaCO_3 = CaHPO_4 + Ca(NO_3)_2 + CO_2. \qquad (2)$$

By the interaction of calcium nitrate and ammonium carbonate (or of ammonia and carbon dioxide), ammonium nitrate and calcium carbonate may be obtained.

$$Ca(NO_3)_2 + (NH_4)_2CO_3 = 2NH_4NO_3 + CaCO_3. \qquad (3)$$

In a subsidiary reaction, accompanying the main reactions in which phosphate is decomposed by nitric acid (1) and (2), hydrofluosilicic acid (4) is formed. It is precipitated with the aid of sodium nitrate (or soda) in the form of sodium silicofluoride (5)

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O. \qquad (4)$$

$$H_2SiF_6 + 2NaNO_3 = Na_2SiF_6 + 2HNO_3. \qquad (5)$$

In the nitric acid treatment of phsophates, the raw material is fully utilized; instead of waste products which are obtained in the sulfuric acid extraction of phosphoric acid (so-called phospho-gypsum) and in the hydrochloric acid decomposition of phosphates (calcium chloride), in the nitric process a fertilizer, calcium nitrate, is obtained. Thus, in this process, the nitric acid is used in a two-fold manner: for the decomposition of the phosphate and for combination with the calcium to form nitrate. In view of the fact that calcium nitrate is less effective than ammonium nitrate as a fertilizer on Central Asian soils, calcium nitrate can be converted to ammonium nitrate by means of ammonium carbonate according to the equation given above (3).

A number of our workers have developed several chemical technological processes for the nitric acid treatment of phosphates, not only for the separate preparation of dicalcium phosphate and calcium nitrate, but also for the preparation of double (nitrogen-phosphorus) and triple (nitrogen-phosphorus-potassium) fertilizers. An example of such a process is the interaction of nitric acid extracts with ammonium or potassium salts (without separating the products of reaction), as a result of which the triple fertilizer "azofos" (abroad "nitrophos") is directly obtained. Equation (6) schematically represents this process.

$$H_3PO_4 + Ca(NO_3)_2 + 2NH_3 + K_2SO_4 = CaHPO_4 + 2NH_4NO_3 + K_2SO_4 \quad (6)$$

The processes in which phosphates are decomposed by mixtures of sulfuric and nitric acid, or mixtures of nitric and phosphoric acids, with the production of a solid phosphorus-nitrogen fertilizer, similar to the production processes for superphosphate (Equations 7 and 8) are also of interest:

$$2Ca_5F(PO_4)_3 + 6HNO_3 + 4H_2SO_4 = 3CaH_4(PO_4)_2 + 3Ca(NO_3)_2 + 4CaSO_4 + 2HF \quad (7)$$

or

$$CaF(PO_4)_3 + 6HNO_3 + 2H_2SO_4 = 3H_3PO_4 + 3Ca(NO_3)_2 + 2CaSO_4 + HF. \quad (8)$$

The fertilizers obtained here, however, contain relatively small amounts of N and P_2O_5.

Other processes for the production of nitrogen-phosphorus fertilizers which could be used by industry without change of apparatus are also being studied. The future use of these processes, as well as the successful solution of the technical problems involved, depends also on how the proposed new forms of complex fertilizers will meet the requirements of agricultural chemistry with regard to the N and P_2O_5 ratio.

Technical-economic and planning estimates show that the processes for the treatment of phosphates with nitric acid should yield phosphorus fertilizers 25-35% cheaper than those obtained by the sulfuric acid methods. Naturally, where nitric acid is being used for the production of nitrates it will be economical to carry out as subsidiary work the decomposition of phosphates and the production of calcium nitrate. In a number of countries the industry has already developed along these lines, and many large factories are already in operation. It should be mentioned that the nitric acid method allows the utilization of lower grade phosphorites than is possible in the sulfuric acid methods, and fluorides are obtained as by-products.

A second promising method, which is of importance for Central Asia, is the electrothermal working of phosphates for the preparation of phosphorus, phosphoric acid, and concentrated fertilizers, as well as phosphates for use as live-stock feeds. The fundamental reactions of this process have been studied in detail by NIUIF, and our industry is already familiar with them [6, 7, 8, 9, 10]. Our country was one of the first to master the process of the electrical sublimation of phosphorus from low-grade phosphorites, and to carry out a deep study of the numerous theoretical problems in the field of themechanism and kinetics of processes connected with this technique, and also the complex process for the preparation of phosphorus with the simultaneous utilization of gases, slag, and ferrophosphor. Below we give the basic reactions of the process for the sublimation of phosphorus from phosphates with the subsequent oxidation of phosphorus and the preparation of phosphoric acid.

$$2Ca_5F(PO_4)_3 + 15C + nSiO_2 = 3P_2 + 15CO + 9CaO \cdot nSiO_2 + CaF_2 - 838 \text{ kcal}. \quad (9)$$

$$2P_2 + 5O_2 = P_4O_{10}. \quad (10)$$

$$P_4O_{10} + 6H_2O = 4H_3PO_4. \quad (11)$$

Reaction (9) is accompanied by the absorption of heat — it is strongly endothermic — but reactions (10) and (11) are accompanied by the evolution of heat — they are exothermic. This presents an opportunity to save electrical energy in the process of phosphorus sublimation

By the interaction of vapors of metaphosphoric acid with lime or phosphates, it is possible to obtain a high-percentage phosphorus fertilizer — calcium metaphosphate — containing up to 66% P_2O_5. The method was first proposed here by Britske [8]:

$$2HPO_3 + CaO = Ca(PO_3)_2 + H_2O \quad (12)$$

or

$$4HPO_3 + Ca_3(PO_4)_2 = 3Ca(PO_3)_2 + 2H_2O\,. \quad (13)$$

An interesting and promising variant is the oxidation of phosphorus by water vapor or liquid water, with the production of elementary hydrogen. This has been studied in NIUIF and in the State Institute of High Pressures, on the basis of the following reaction:

$$P_2 + 5H_2O = P_2O_5 + 5H_2\,. \quad (14)$$

The hydrogen separating in the furnace, together with the phosphorus, also reacts with the water vapor to form hydrogen and carbon dioxide:

$$CO + H_2O = H_2 + CO_2\,. \quad (15)$$

Further, hydrogen combines with nitrogen to form synthetic ammonia:

$$N_2 + 3H_2 = 2NH_3\,. \quad (15a)$$

By the interaction of ammonia and phosphoric acid, ammonium phosphate may easily be obtained:

$$H_3PO_4 + NH_3 = NH_4H_2PO_4\,. \quad (16)$$

The result is a combination of two important chemical processes — the preparation of phosphorus and phosphoric acid, and the synthesis of ammonia. As a result of the combination there is a saving in electrical energy in the preparation of hydrogen, since this is obtained from the energy of oxidation of the phosphorus by water. This complex of processes is of interest not only because the development of hydroelectic construction makes possible the raising of this question, but also because the electrochemical method permits the utilization of low grade phosphate raw materials and the preparation of highly concentrated and pure phosphoric acid, which facilitates and simplifies its further industrial treatment and conversion to concentrated fertilizers.

Other thermal and thermal-alkali methods for the treatment of phosphates, for example, baking or fusing with natural alkalies, salts or magnesium silicates, the treatment of phosphates with water vapor under high temperature for the removal of fluorine, the preparation of metaphosphates and pyrophosphates, and so on, should be evaluated, not only from the point of view of their technical and economic suitability for production from local raw materials, but also for their agricultural chemical efficiency. Large scale field trials on citrate-soluble types of fertilizers have not yet been carried out on Central Asian soils.

The following are the main reactions on which these processes are based:

The preparation of thermophosphates*:

$$2Ca_5F(PO_4)_3 + \underbrace{3Na_2CO_3}_{(3Na_2S + SO_2)} = 2Na_2O \cdot 10CaO \cdot 3P_2O_5 + 2NaF + 3CO_2. \quad (17)$$

The preparation of fused magnesia phosphates:

$$Ca_5F(PO_4)_3 + 3MgO + 6SiO_2 = 4CaO \cdot 3MgO \cdot 3PO_4 \cdot 6SiO_2\,. \quad (18)$$

The defluorization of apatite:

$$2Ca_5F(PO_4)_3 + 2H_2O = Ca(OH)_2 \cdot 3Ca_3(PO_4)_2 + 2HF\,. \quad (19)$$

As can be seen, this reaction is accompanied by the displacement of fluorine from the crystal lattice of apatite, and its replacement by hydroxide. The latter process is of interest because the transformation of P_2O_5 into a form easily assimilated by the plant is carried out by a process in which the only chemicals used are water vapor and silica.

Of the nitrogen fertilizers, the most useful type is ammonium nitrate, the physical properties of which have markedly improved as a result of granulation and the introduction of modifying additives (the caking and hygroscopic properties are markedly reduced). In order to improve the physical properties, other formulas have been proposed, and also a number of variations of the industrial process. The organic additives which have been used for a number of years to improve the physical properties of ammonium nitrate have now been replaced by inorganic ones.

Because of their low efficiency, sodium and calcium nitrates are of lesser value on Central Asian soil

* In the Institute of Chemistry and Metallurgy of the Kazakh Academy of Sciences, Bekturov studied the preparation of thermophosphates by using sodium sulfate and carbon (i.e, sodium sulfite) instead of soda [11].

than in other districts, and their low nitrogen content (12-17 %) in comparison with ammonium nitrate (35%) should stimulate the development of the latter.

Until recently the production of calcium cyanamide (alkaline nitrogen fertilizer) has been regarded as uneconomical be cause of its high power requirements, its low nitrogen content (from 18 to 20%), and the necessity of taking precautions to avoid poisoning of animals where it is used. Since calcium cyanamide is not only a nitrogen fertilizer, but also a herbicide (an anti-weed agent) , and in recent years has begun to be used successfully as a defoliant for cotton (it assures the rapid removal of leaves for the subsequent use of mechanical pickers) the question of the development of calcium cyanamide production on a large scale should be examined from the technical and economic points of view, with the prospect of new hydroelectric constructions being taken into consideration.

The development of the production of synthetic carbamide (urea), one of the most efficient and the most concentrated of the known nitrogen fertilizers, is mainly dependent on the development of the synthesis of ammonia, the subsidiary preparation of concentrated carbonic acid, and the economical production of urea and its solutions in liquid ammonia. These may be of interest as concentrated liquid fertilizers (having insignificant vapor tension in comparison with liquid ammonia), or as intermediates for the preparation of complex fertilizers and for the ammonization of superphosphate with the admixture of urea [12].

The most useful form of potassium fertilizers for Central Asia are those in the form of high-potassium-content salts—chlorides and sulfates, and in the future, possibly, potassium nitrates and phosphates. Potassium salts of low potassium content usually contain sodium chloride and other salts, which raise the saline content of the soil, which is naturally undesirable on saline soils.

Mixtures of fertilizers are advantageous, and for this it is necessary to ensure the neutrality of the phosphates used as components. For example, superphosphates should be previously neutralized with lime and ammonia before being mixed with ammonium nitrate. A suitable phosphate component of fertilizer mixtures is precipitated dicalcium phosphate, because of its neutrality, ease of dispersion, and good physical properties.

What are the main scientific and production tasks in the near future?

It is necessary to establish the efficiency on Central Asian soils of the citrate-soluble forms of phosphates contained in defluorized, fused and alkaline phosphates and also in meta and pyrophosphates, the production of which does not require the consumption of mineral acids and may be carried out even on phosphorites which are rich in magnesium carbonate and silicic acid. The study of this question should be related to theoretical investigations on the mobility of various forms of phosphates in gray desert soils and on their absorption by the plant; this depends on their degree of particle dispersion, which is connected with their granulation. Here, a theoretical investigation of the nutrient substances which are assimilated by plants(not connected with the soil) is of great interest. The study of the optimum proportions of nitrogen, phosphorus and potassium for pre-seed and supplementary fertilizers should be studied more intensely and in a more extended manner in order to solve the question of the production of complex and mixed fertilizers meeting the requirements of the cotton, alfalfa, sugar-beet, fruit and other crops.

An intensified study should be continued on organic mineral fertilizers based on the treatment of carbons, peat, plant cellulose and other natural organic materials with phosphoric and nitric acid, ammonia, and so on, in order to determine their efficiency, and especially to discover the part played by humus compounds as growth promoters. The problem of the combined use of fertilizers and growth stimulators is of great interest. The study of the requirements of Central Asian agricultural crops for microelements, boron, manganese, zinc, etc., should be continued. For a complete and rational utilization of the Kara-Tau phosphorites an all-around increase in the study of the methods for their mechanical and chemical enrichment should be carried out. As well as this, the study of the efficient production of thermal and alkaline phosphates should be intensified, especially thermal phosphates, fused phosphates, meta- and pyrophosphates and also defluorized phosphates. The use of local mineral resources as a supplement for cotton, and in order to reduce the transport costs over long distances, the production of "ammofos" from the Kara-Tau phosphorites, should be introduced in order to increase the physical properties of superphosphate; the mastering of the processes of ammonization by means of ammonia and ammonium salts should be hastened.

It is necessary that the production of dicalcium phosphate (precipitated) with the subsidiary preparation of ammonium nitrate from the nitric acid decomposition of the Kara-Tau phosphorites should be mastered. At the same time, the agricultural, chemical, and economic suitability of the double and triple fertilizers containing phosphorus, nitrogen, and potassium (of the types "azofos" or "nitrofos" in the granulated form) should be determined. Attention should also be paid to the study of the suitability of methods of producing nitrogen-

phosphorus fertilizers by simplified technological processes in which the phosphates are decomposed by mixtures of nitric and sulfuric acids (similar to superphosphates).

A process which shows considerable promise is the electro-thermal treatment of unenriched Kara-Tau phosphorus obtained into phosphoric acid, concentrated fertilizers, and phosphates for foods and feed-stuffs. Here a detailed study is required for the processes in which phosphorus is oxidized by steam and by liquid water with the production of elemental hydrogen, and the subsequent synthesis of ammonia, with the object of combining the latter with phosphoric acid to form ammonium phosphate.

Investigation should be continued on the complex processes in which phosphorus is distilled with the simultaneous preparation of calcium carbide or earth-clay cement and also other methods for the utilization of carbon monoxide, ferrophosphor and slags.

In the field of nitrogen fertilizers, work should be continued on the all-round improvement of the physical properties of ammonium nitrate in order to reduce further its tendency to cake — its hygrocropicity — and to remove its tendency to increase in volume with higher temperatures, and to obtain a granular product. With this aim it is desirable to intensify the analysis of the physico-chemical properties of different modifications of nitrate of ammonia and the influence of various additives, moisture, tempering (rapid cooling) and other treatments. It will be useful to examine from the technical and economic viewpoints the question of the future synthesis of urea from ammonia and and carbon dioxide under Central Asian conditions for use as a high percentage fertilizer and important technical products.

With the aim of preparing high-grade and chlorine-free potassium fertilizers (the latter for some agricultural crops), it is expedient that methods of production of potassium sulfate, potassium nitrate and potassium phosphate on a pilot-plant scale should be mastered. It will be necessary to carry out a number of supplementary physico-chemical investigations of the equilibrium systems and reaction kinetics of the processes occurring when phosphates are decomposed by acids, and also in the processes of baking and fusing them with alkaline compounds and with aluminium silicates. The possibility should be examined of using local resources for gypsum (and further possibly for phospho-gypsum) for the improvement of saline soils and the use of organic substances to improve their structure.

Attention should also be given to the agro-technical and economic study of conditions for the application of mineral fertilizers (phosphates, ammonium and nitrate salts, triple fertilizers) in the liquid state, which have been successfully tested by NIUIF in field experiments on northern soils as suggested by Britske [13].

The research and experimental work enumerated above could not possibly be carried out if the solution of these problems was entrusted to only one institute or one Academy of Sciences, even with a large number of highly qualified workers. Only by planned collaborative team-work, based on a clear division of the work, and in addition with cooperation and mutual aid between the workers in science and industry, will it be possible to solve the problems presented here.

Today we may note with pleasure that in this great work, together with institutes, laboratories, experimental stations of the All-Union and Republican Academies of Sciences, in recent years factories and collective farms have cooperated. We note with pleasure that in recent years steps have been taken to found a fertilizer laboratory in the Uzbekh Academy of Sciences, that already a number of experimental stations are working in Central Asia in the field of agricultural chemistry and in this work practically all the fertilizer factories of Central Asia take part. I hope that the reading of the present paper will help to set forth the most important themes, will aid in their critical selection and will bring together the creative forces for their fulfilment.

In closing I should like to mention that the reading of this report at a combined session of the Uzbekh Academy of Sciences and the Division of Chemical Sciences of the Academy of Sciences USSR was not the result of an attempt to meet local requests of our Uzbekh comrades, but is the result of deeper and weightier considerations. These are based on the fact that it is just in Central Asia and Southern Kazakhstan that the business of producing and applying fertilizers must be devoloped both qualitatively and quantitatively at a high scientific level; because here the the natural resources of power and raw materials are large, and fertilizers are both effective and are needed in large quantities. It is natural, therefore, that this problem should attract not only Central Asian but also all Soviet chemists, agronomists, engineers, who on the basis of Stalin's tradition of friendship of the peoples, unity of theory and practice, using the growing interrelationship between chemistry and biology, wish to see the best and most progressive and most economical fertilizer production methods and their wide application in agriculture.
If the Central Asian agricultural industry has reached the first place in the world for cotton productivity, then we

wish to see it going forward with all other crops on the basis of a wide utilization of chemical methods in agriculture, and the application of leading methods of agro-technique, irrigation, and the latest achievements of scientific organization in agricultural production.

For, according to the Directives of the 19th Party Congress, the fulfilment of the 5th Five-Year Plan will be one of the greatest steps forward on the road to development from Socialism to Communism. In his outstanding work on economic problems of socialism in the USSR, Comrade Stalin points out that according to the basic economic law of socialism, provision for the maxiumum satisfaction of the constantly growing material and cultural requirements of all society must be effected by the continuous growth and improvement of socialist production on the basis of efficient techniques.

It is useful to remember that the mineral fertilizer industry is one of the largest branches of the chemical industry. The world production of fertilizers at present amounts to more than 35 million tons per year. It continues to grow rapidly both qualitatively and quantitatively. Its growing importance for our country needs no proofs. Naturally, this branch of chemical industry must be developed in the Soviet Union on the basis of the latest achievements in science and technology. I should like to express my confidence that Soviet chemists in close cooperation with biologists and workers in the chemical and agricultural industries will fulfill with honor the Directives of the 19th Party Congress and in this way make their small contribution to the work of building a communist society.

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RECENT DEVELOPMENTS IN THE PHYSICO-CHEMICAL INVESTIGATION OF COTTON FIBER*

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In the discussions of the 19th Party Congress and its Directives on the Five-Year Plan, great attention was devoted to the further development of cotton growing in the USSR. A considerable proportion of cotton is already beginning to come from new cotton-growing regions. The level of production of the cotton plant in the Soviet Union greatly exceeds that of capitalist countries. Last year the amount of cotton fiber worked represented a great increase over that of pre-war 1940. In 1955, the production of raw cotton in the USSR will exceed 1950 by 55-65%.

As a result of the introduction of new varieties of cotton and improvements in the technique of their cultivation, the quality of the fiber has been improved with regard to length, strength, and variety. Soviet cotton is the best in the world. However, we must continually strive to increase the quality of cotton, to improve the varieties with regard to harvesting, and to increase the boll size. There is no doubt that this huge project of the Five-Year Plan for the improvement of the production of cotton and cotton fiber will be fulfilled. The mechanization of agricultural work is developing rapidly, and the science of cotton growing makes it possible to gather from both new and already familiar fields additional millions of tons of high quality cotton fiber.

In view of this huge scale of production of cotton fiber and the large future development which is promised, scientific research institutes devoted to the cotton plant and to cotton fiber must consider two large problems. First, improvement of the quality of cotton fiber by means of selection. Second, the discovery of more rational ways of utilizing different varieties by making a detailed study of the properties of these varieties. It is natural that these problems and their many component parts are being worked out by a great army of Soviet investigators, and already great successes have been attained.

In the present report, our aim is to explain a new proposal in the development of these two problems. This proposal is concerned with the development of new requirements for cotton fiber. It is proposed that additional chemical, or strictly physico-chemical requirements should be instituted for cotton fiber. It is well known, for example, that the fatty and waxy constituents of cotton fiber have a great influence on the preliminary treatment of the fiber and on its spinning; and also that in the finishing of cloth before dyeing, the most difficult particles to wash out of the cloth are the natural impurities in the fiber, natural congeners of cellulose. The content of these impurities, or strictly speaking, the chemical composition of different fibers, as we know, is different for different varieties of the cotton plant.

The chemical composition, for example the content of fatty and waxy substances, plays an essential role in the preparation of special materials such as cord for automobile and aeroplane tires. The quality of the latter is highly dependent on the moisture content of these cords.

The durability of articles prepared from cotton fiber naturally depends almost entirely on the technological properties of the original fiber. In the preaparation of high quality articles, it is necessary to use fibers possessing specific characteristics. The industrial treatment also depends upon these properties. It is quite obvious that a knowledge of only the final or original properties of the fiber is insufficient. It is necessary to know the properties of the fiber under all the conditions of its utilization, and to know how these properties change under different conditions.

All this clearly shows that the time has come to institute for fiber, in addition to the existing requirements for length, fineness, and strength, further physico-chemical standards. In other words, in the introduction of a new variety, the selector must take into consideration not only the yield and the essential qualities enumerated above, (length, fineness, and strength), but also of the chemically valuable properties of the future fiber, and select chemically useful varieties from which to breed. Furthermore, when a given variety of fiber is used in the manufacture of certain articles, the technologist must know the physical, chemical, and mechanical characteristics of this fiber, not only in its original condition, but also under the conditions in which it will be used.

* Paper read at the joint session of the Division of Chemical Sciences, Academy of Sciences, USSR, and the Academy of Sciences, Uzbek SSR, October 25, 1952, Tashkent.

Only in this way will it be possible to make a rational selection of the method of treatment and to guarantee the preparation of cotton articles having the required qualities. In order to develop these new, as we have termed them, physico-chemical requirments and to relate them to the technological treatment of fiber, team-work by chemists, especially by chemists working in the extensive field of high-molecular-weight compounds, selectors and technologists is necessary. It is necessary to have theoretical and practical cooperation between these and many other related disciplines dealing with cotton fiber, with cellulose, with artificial cellulose fibers and even with cellulose ethers. Work connected with these problems has been, and is being, carried out in many research institutes and laboratories of the Union.

The Uzbekh SSR is one of the most favorable regions for the cultivation of cotton in the Union. It is therefore reasonable to develop the work on the investigation of the cotton plant, including the work on the physico-chemical investigation of cotton fiber, here, in Uzbekistan.

The carrying out of such investigations in our Republic is facilitated by the proximity of selection stations and the possibility of close co-operation between our workers and workers in these stations, as well as in the many institutes in Tashkent working on cotton fiber.

The work of Surova and Zakoshchikov, Ivanova and Kurennova, Rytikov, Korzheniovsky, and Marchenko, in this field carried out 20 years ago was also done in Uzbekhistan [1]. After this work, which embraced a few selection varieties, no serious systematic chemical investigations were carried out on cotton fiber.

Our comparative studies on natural cellulose (cotton fiber) and on hydrated cellulose carried out in 1946 to 1950 in co-operation with Kargin, the basic results of which we reported to the 7th Conference on the Chemistry and Physical Chemistry of High Molecular Weight Compounds in Moscow in June 1952, is the basis of the present work. This threw additional light on the properties of chain-like cellulose macromolecules and made it possible to suggest that "cellulose is a loosely packed material, which results from the great rigidity of the cellulose chains and the difficulty of displacing them. This corresponds with its high elastic properties and its great sorptive power for water. Under any conditions which decrease rigidity and increase the mobility of the cellulose chains, the packing becomes more dense, and this results in a reduced sorption of water. These transitions are of a continuous nature" [2].

We studied the chemical composition, the degree of polymerization and the sorption of fiber at various periods of vegetation and we determined the breaking strength and also recorded deformation curves under different humidity conditions. The same fiber samples were examined in the Institute of Agriculture of the Academy of Sciences, Uzbek SSR before being subjected to several standard industrial tests. The electrical properties of the fibers and of the raw material were studied in the Physical Technical Institute of the Academy of Sciencs, Uzbek SSR mainly with the object of establishing the theory of hygrometers. For these tests, previously labelled pods from the first positions of 2-3 sympodia were collected every five days. After the necessary cleaning, the fiber was examined chemically.

Many workers have been interested in the composition of cotton fiber from different selection varieties. According to a number of investigators, the chemical examination of cotton fiber from different selection varieties, when all the samples are fully matured, does not disclose any difference in the chenical composition which might be utilized to characterize one fiber or another. On the other hand, it has been shown for six American varieties of mature fiber that significant differences are found in the chemical composition of different varieties (cellulose, reducing sugar, wax, etc.) Such contradictory reports are numerous in the literature.

The aim of the present work was to investigate the rate of change in the proportion of cellulose to other materials and yields of cellulose from different varieties of cotton plant according to the vegetation period. Chemical analysis was, for the present, confined to the determination of the main components of the fiber, in order to compare varieties and to measure the rate in change of the content of cellulose, fats and waxes, pectin substances, pentosans, reducing substances, and ash. There are several methods in the literature for the determination of cellulose in the fiber of the cotton plant (Cross-Bevan, Müller, Shalbe-Robinov) [1]. We used the method of Corey and Gray [1] which is different from the method of Shalbe-Robinov in that there is no bleaching, and it is therefore less drastic than the Shalbe-Robinov method. As has been confirmed in the literature, cellulose obtained by the Corey and Gray method may be used for the most precise scientific investigations.

Pectin substances were determined by a modified Viktorov method in the form of calcium pectate [4]. The pentosans were determined by the method of Tollens by treating the fiber with 12% hydrochloric acid, distilling off the furfural formed and precipitating it with phloroglucinol [5]. For the determination of reducing sugars, a weighed sample of fiber was treated with distilled water and boiled under a reflux condenser for four hours; the reducing substances were then determined in the extract by the method of Issekuts. The ash was de-

determined by igniting the fiber to constant weight in a porcelain crucible at [illegible]°.

In all the determinations allowance was made for the relative humidity of the laboratory air. The content of moisture in the fiber was determined from the relative humidity and the [illegible] and the absolute dry weight of sample calculated. The results of all the analyses are based on this absolute dry weight. Some results of the mechanical investigations of seven selection varieties are shown (Figs. 1-5).

From Figure 1 it is clear that for the same growth of fiber different varieties of cotton have different cellulose contents, this discrepancy becoming smaller toward the end of vegetation, but not falling to zero. Eighty-day fibers of different sorts also differ from one another in their cellulose content. The growth of cellulose in all varieties is significant at the beginning of vegetation and slows down toward its end. In most of the varieties 85-90% of the total accumulated cellulose is built up in 40 days of the vegetation period, the further accumulation being at a slower rate.

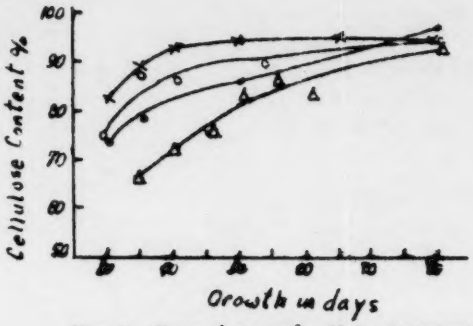

Fig. 1. Dependence of cellulose content in different varieties of cotton, on ripeness: Δ – 1306 DB ● – S-450-555; o – 18819; × – 3210.

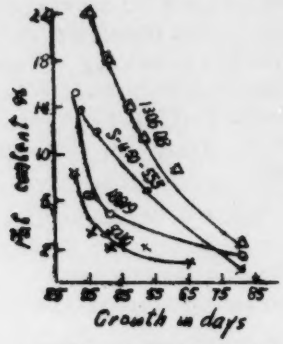

Fig. 2. Dependence of fat and wax content in different varieties of cotton, on ripeness.

There are two characteristic differences in the accumulation of cellulose between different varieties. In variety 3210 after 40 days, 90% of the cellulose had been accumulated, but in variety 108-F, 107-F, S-460 and others, only 80 to 85% of the cellulose had been accumulated in this period. [illegible] this difference in growth of the amount of cellulose depends also upon the agricultural, technical and other conditions under which the plant is grown; but the influence of variety is clear.

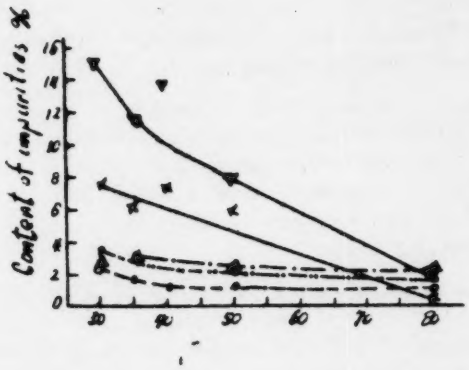

Fig. 3. Dependence of impurities content in fiber of varieties S-450-555, on ripeness; o – [illegible]; ● – pectins; ○ – ash; × – reducing sugars; ✓ – fat and wax.

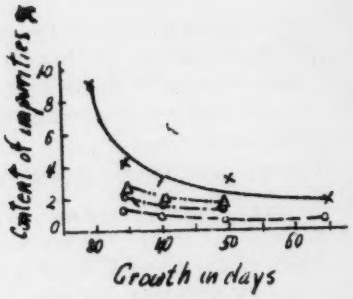

Fig. 4. Dependence of impurities content in fiber of variety 3210, on ripeness, o – pectins; ● – ash; Δ – pentosans; × – fat and wax.

It appears to us that this difference is connected with the period of maturing of the cotton plant and it is possible indirectly to predict the date of opening of the pods 30 to 40 days ahead. This connection between variety and chemical composition evidently exists not only in relation to the accumulation of cellulose, but is also shown by the other components of the fiber. For example, by the relative decrease in the fatty and wax components of the fiber,* which is evident from Figure 2, where the greatest rate of change occurs with variety 3210.

The other figures show changes in different impurities of the cellulose with ripeness of fiber for three

* In our experiments the fatty and wax fraction is defined as the total loss in weight on ethanol-ether extraction.

TABLE

Growth of cotton in days	Cellulose viscosity in centipoises			
	Fuadi	Maarad	No. 0491	No. 246
30	1080	652	1058	1377
45	2557	1194	1142	2036
70	3550	1316	2243	3028

selection varieties of the 1951 harvest. From these figures it is clear that a marked fall in the content of pectin substances, pentosans, and ash in all varieties concludes at the 35th to 40th day. Up to the 60th day from the day of flowering the content of these substances in the fibers is within the limit 1 - 2% but varies with different varieties. In 25 - day growth the content of these substances reaches 4%.

As will be seen from these graphs, each variety of cotton plant has its own kinetics of fiber development, that is the kinetics of change in the chemical composition of the fiber in the vegetation period.

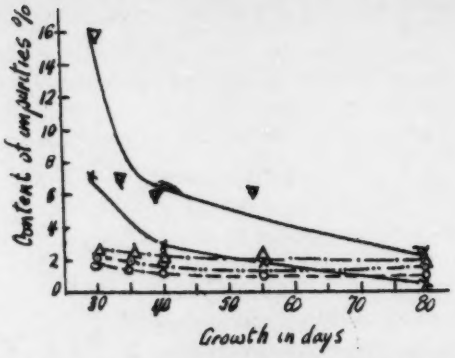

Fig. 5. Dependence of impurities content in fiber of variety 18819, depending on growth: o —pectins; • —ash; Δ —pentosans; × —reducing sugars; ▼ —fats and wax.

Samples of purified cellulose obtained by the method of Corey and Grey were used to determine the degree of polymerization. It is known that the main reactions in the formation of high polymers are polymerization and polymer condensation, and as a result of these the long molecular chain is produced. The bio-chemical synthesis of cellulose, which has not been fully elucidated, proceeds by one of these reactions. If we assume that the biochemical synthesis is due to polymerization, then the molecular weight of the cellulose in the process of fiber growth should not change. On the other hand, if the process is one of condensation, the molecular weight of the cellulose should change with the growth of the fiber. Therefore, in the elucidation of this problem, determination of the molecular weight of cellulose during the process of vegetation of the fiber is one of the main methods; and this process is important in the chemistry of the cotton plant.

That the maturing of the fiber is a process in which cellulose is accumulated has been confirmed by the results of chemical analyses carried out previously by Ivanova and Kurennova. They showed that the amount of cellulose deposited in the walls of the cotton fiber changes with the ripening of the pod [1]. Surova has observed that the degree of polymerization of four varieties of cotton increases as the fiber matures. Moreover, for one and the same degree of maturity of fiber differences were observed in the viscosity of the cotton fiber cellulose for different selection varieties of cotton (see table).

The concept of the maturity of cotton, which is always identified with the opening of the pods, is in actuality more complicated. The moment of opening of the bolls, considered as the sign of the end of ripening of all its elements, in the case of cotton may not coincide with complete deposition of cellulose in the fiber; on the contrary, the deposition of cellulose may precede opening of the pods. Thus, it is necessary to distinguish maturity of the bolls from maturity of the fiber.

There is some data in the literature which indicate that the molecular weight of the cellulose increases with the growth of the fibers. Therefore, if the rate of change of the molecular weight over the period of vegetation were systematically followed, it would be possible to determine how the molecular weight depended on time, and this would make it possible to relate the molecular weight to the degree of maturity of the cotton fiber.

Moreover, a large difference in the properties of cotton fiber of different varieties and of different degrees of maturity and growing under different climatic and agronomical conditions would be determined by differences in their molecular weights; and here the determination of the relationship should be carried out. The establishment of the laws of change in the degree of polymerization of cellulose of different varieties in the vegetation period would enable problems on the rate of maturing of the cotton plant to be explained by the conditions of biochemical synthesis of cellulose.

In our experiments the degree of polymerization was determined by the viscosity method in an Ubbelohde apparatus under the pressure of pure nitrogen, the precautions with regard to oxygen pointed out in the papers of Golova and Ivanov, Shults, Guzeman, Dzhoiner, and others [6], being taken.

The results of the experiments are shown in Figures 6 and 7. As will be seen, results of measurements made in 1951 are different from the results obtained in 1952 on the same samples, which had been kept under laboratory conditions for about a year.

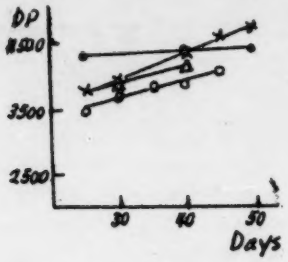

Fig. 6. Degree of polymerization for samples: —×—460; o — S—3210; Δ—137—F; o—108—F

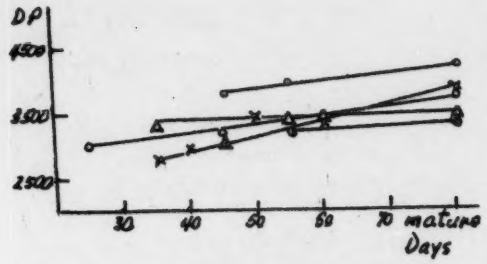

Fig. 7. Degree of polymerization for samples: ●—18819; o—450-555; ● 108 - F × — 1306—DB ; Δ— S -3210.

Values for the degree of polymerization determined on cotton cellulose after it had been stored for a year were much lower than those obtained initially. Evidently, atmospheric conditions and duration of storage have some influence on the degradation of cellulose.

Moreover, in these two series there are some figures which do not support the general tendency of the remaining ones. This evidently must be regarded as a weakness in our experiment and generally in the method of determining the molecular weights of polymers, but a careful analysis of the results clearly shows the presence of definite relationships in the change of molecular weight of cellulose in the samples we have studied.

In all the samples we examined, an increase in the degree of cellulose polymerization as the fiber matured was observed. For the same growth period, the increase in molecular weight differed with different varities of cotton; in other words, the law governing the growth of the degree of polymerization is different for different selection varieties. In the same way the magnitude of the degree of polymerization also differs. Variety 3210 as is known, is the most rapidly maturing of all the samples we examined, but as will be seen from the results given, the magnitude of the degree of polymerization remains practically unchanged with growth. It is probable that for the rapidly maturing varieties the degree of polymerization quickly reaches the normal value in the early stages of development of the fiber and, therefore, remains constant during the further growth of the fiber. Therefore, for unripe growths a constant molecular weight after 25 to 30 days growth, with a relatively high absolute value, is evidence of the rapid maturing of the given selection variety of the cotton plant.

As well as determining the degree of polymerization of the cellulose, we determined the hydrogen ion concentration of the sap from the cotton pods of a 25 - day old growth of variety 108 - F. The determination was carried out by two methods: the electrometric and the indicator method.

In the first case we used both the hydrogen and the quinhydrone electrodes. In determinations with the hydrogen electrode the pH was 6.1 and with the quinhydrone, 6.8 - 6.6. The determination by the indicator method gave a value of pH 6.0 - 6.1. From the results obtained it may be assumed that the value was pH 6.0 - 6.1, i.e. the development of the fiber takes place in a weakly acid medium.

The sorption studies and the mechanical behavior examination were carried out on cotton fiber freed from impurities. The sorption was determined by the method of the vacuum sorption balance with a sensitive quartz barrel in a thermostat. The water for the sorption and the samples of cotton fiber were carefully degassed before the sorption isotherm was recorded [2]. The results of the sorption measurements are given in Figures 8, 9 and 10.

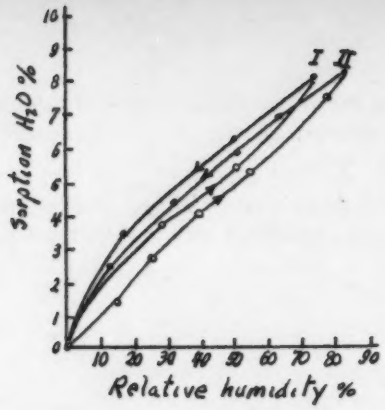

Fig. 8. Sorption and desorption of water on cellulose of 65-day and 25-day cotton, variety 3210, at 25°; o – sorption; • – desorption; (I) 25-day; (II) 65-day.

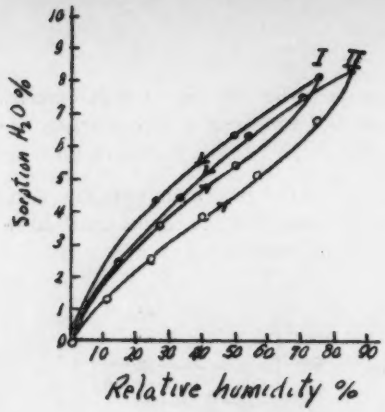

Fig. 9. Sorption and desorption of water on cellulose of mature and 25-day cotton variety 18819, at 25°; o – sorption; • – desorption; (I) 25-day; (II) mature.

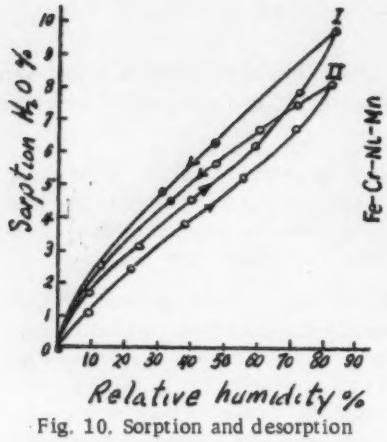

Fig. 10. Sorption and desorption of water on cellulose of 60-day cotton, variety 108-F at 25° and variety S-460; o – sorption; • – desorption (I) 60 day 108-F; (II) 60 day S-460.

In all the sorption experiments the establishment of sorption equilibrium was confirmed by recording the sorption kinetics. Complete equilibrium was established after a few hours, or after days. Experiments carried out with fiber and with cotton wool without preliminary removal of air from the sorption apparatus gave slow kinetics of sorption, evidently because of "air pockets", and retarded diffusion at the phase boundaries. On the basis of a series of similar experiments carried out in connection with the Republican Conference on Cotton Driers organized by the Academy of Sciences, Uzbekh SSR, the advantages of the layer type of drier construction proposed by the Energetics Institute of the Academy of Sciences, Uzbekh SSR, were shown.

Our investigations on fiber mechanics were devoted to a study of the mechanical properties (deformation and breaking load) of cotton cellulose in relation to humidity, variety, and time of vegetation. In order to obtain trustworthy dynamometric results, it is necessary to use completely purified cellulose preparations from which all impurities have been removed, especially traces of moisture, since traces of the latter have a powerful influence, and affect the physico-mechanical properties of the material. In such an investigation it is naturally not possible to use existing dynamometers which are intended for testing fibrous materials. For this purpose Kargin and Usmanov have constructed a special electric vacuum dynamometer which permits the examination of fiber under any given humidity condition, as well as in a completely dry state, under a high vacuum [2].

Thus in this work we first studied the relationship between the mechanical properties of cotton fiber and its humidity over a wide humidity range. We examined samples of varieties 3210, 18819, and S-460 at different vegetation periods. For every vegetation period, experiments were carried out on the dry fiber and also at relative humidities of 15, 38, 60 and 85%.

Figures 11 and 12 give deformation curves for absolutely dry and moist fiber, variety 3210, of 35- and 45-day growth, depending on load. As will be seen from the curves, absolutely dry fiber has almost a straight-line deformation up to the breaking point. Such a fiber undergoes only slight extension on breaking, and corresponds to the glasslike state of cellulose, but the presence of an appreciable deformation in completely dry cellulose is evidence of the loose packing of this substance in the glass-like state.

The considerable deformation suffered by fiber in the moist condition may evidently be explained in two ways: [1] by the plasticizing effect of moisture on the fibre with a change in the intermolecular forces; and [2] by a change in the flexibility of the cellulose chains. The mechanism governing the increase in deformation with the increased moisture might usefully be the subject of a discussion. As has been said above, cellulose chains are rigid, and this chain rigidity should lead to the minimum deformation of rigid polymers. It also determines the presence of loose packing, since from rigid rods - if we roughly imagine the molecular model in the amorphous state - it would be possible to obtain densely packed material. This results in the presence of much deformation, even in the absolutely dry state, and the large sorption capacity of cellulose materials, as well as the high rate of diffusion of gases and vapors through them [9].

Consequently, from our work on the mechanical behavior of cellulose fibers carried out over a wide range of moisture content, the conclusion may be drawn, and this evidently is also applicable to polymers with rigid chains, that for this class of polymer a secondary deformation mechanism operates, though for flexible rubber-like polymers the deformation is determined only by the great flexibility of the chains (for crystalline polymers by the remelting of the crystals). For rigid cellulose-like polymers the deformation is determined by the flexibility and by the presence of loose packing. The deformation process of rigid polymers consists of two mechanisms. The elastic component is evidently determined mainly by the loose packing, and the highly elastic component by the flexibility of the chains. As to the explanation for the effect of moisture on the increase in deformation, as has been shown, our experiments carried out in co-operation with Kargin have demonstrated that water changes the density of cellulose packing only at high temperatures (200°). Therefore water mainly acts through its effect on the flexibility of the chains, and by its plasticizing action.

The variations in the mechanical properties of several varieties of cotton cellulose with moisture content at 20° is shown in Figures 13, 14, and 15. Each point on the diagram represents the mean deformation and load value obtained from 100 to 120 individual measurements.

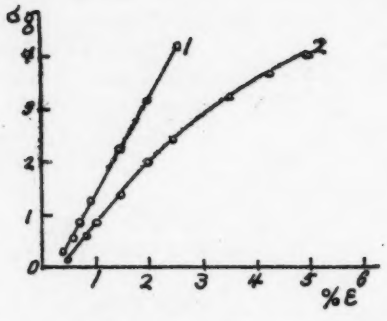

Fig. 11. Deformation of 35-day cotton fiber, variety 3210, depending on load. 1) Absolutely dry fiber; 2) fiber at 85% humidity.

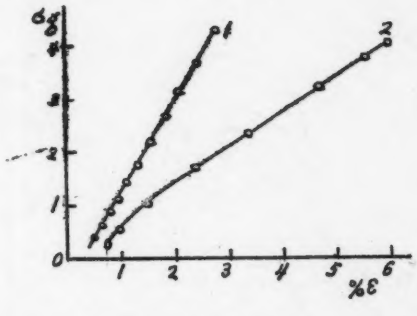

Fig. 12. Deformation of 45-day cotton fiber, variety 3210, depending on load. 1) Absolutely dry fiber; 2) fiber at 85% humidity.

These curves show that there is a fairly strong relationship between the mechanical properties and vegetation period of cotton fiber. Indeed, as the pod ripens, as well as an increase in the breaking load, there is also observed an increase in the deformation. The increase in the deformation with the fiber age is evidently caused by a thickening, that is by the deposition of cellulose in the fiber. It is of interest to note that in sample 3210 the breaking load, that is its strength in comparison with other varieties, increases only slightly with the degreee of maturing of the fiber. Thus, for example, the breaking load of absolutely dry 35-day fiber is equal to 4.2 grams and of 55-day, 4.5 grams. Evidently this is connected with the fact that variety 3210 is a more rapidly maturing type than the others which we have investigated. Evidently, the deposition of cellulose takes place rapidly and the fiber strength reaches a maximumvalue at an early period of growth, and changes only slightly during the remainder of the vegetation period. As will be seen from the results given, the presence of moisture in cellulose fiber considerably changes its mechanical behavior picture, an increase in moisture causing a fairly smooth and notable

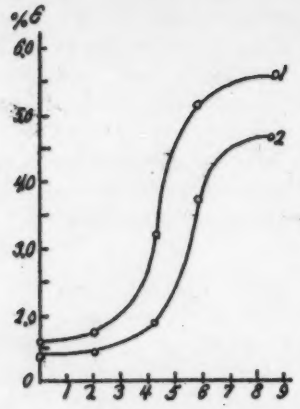

Fig. 13. Relation between the deformation of cotton cellulose, variety 3210, with the moisture, for different vegetation periods: (1) 35-day cellulose; (2) 45-day cellulose.

increase in its breaking strength and a more marked increase in its length. In contrast to natural fibers, artificial fibers in the moist state, as is known, not only do not increase in strength but, on the contrary, suffer a reduction of 50 - 60%. This difference in the behavior of natural and artificial fibers may evidently be explained by the fact that cotton fiber in its nature is strongly oriented and possesses in comparison with viscose rayon some degree of polydispersion, and also spirally disposed chains. It consists of the largest types of macromolecules, not differing greatly among themselves in molecular weight, unlike artificial fibers. This difference confers on cotton fibers exclusive properties, including its power of increasing in strength with increased moisture content. As regards the lengthening of fiber with increase in moisture content, with an initial increase in the moisture content of absolutely dry cellulose there is a slight increase in length; with a further increase in the moisture content of the fiber, within the moisture limits of 4.0 - 6.0% there is a marked increase, which is followed by a slowing down.

Thus the deformation-moisture graph for cotton fiber is S-shaped, similar to the type previously obtained for viscose rayon [7]. These two types of cellulose have this in common; the region of rapid growth in the deformation corresponds to the same relative moisture content.

If we compare our results with those of Mikhailov and Kargin [8] on the flow of highly swollen cellulose fiber, then we obtain a picture which has a great similarity, at least in its external form, to the well-studied picture of the deformation change with temperature under different time conditions. In fact, whereas in the experiments of Mikhailov and Kargin on highly swollen (wet) fibers the viscous state of flow was reached, in our experiments over a wide range of moisture content, limits were indicated for the appearance under the given time conditions (the deformation limit was reached in 2 minutes) of highly elastic and glasslike states of cellulose; this elastic state of the fiber appears at a much lower temperature than vitrification which, as is known, takes place at a higher temperature, about that which cellulose decomposes. Consequently, the water absorbed by cellulose under ordinary atmospheric conditions changes it from the glasslike state and, as a result makes possible the appearance of those highly elastic properties at normal temperatures which are so valuable in the technology of textile threads.

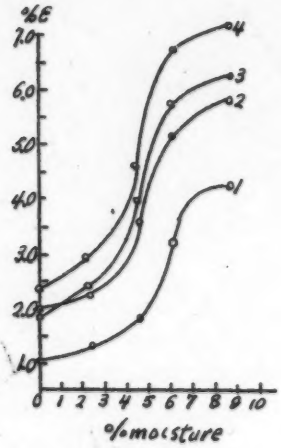

Fig. 14. Relation between the deformation of cotton cellulose, variety 18819, with the mositure at different vegetation periods. 1) 30-Day cellulose; 2) 40-day cellulose; 3) 50-day cellulose; 4) mature cellulose.

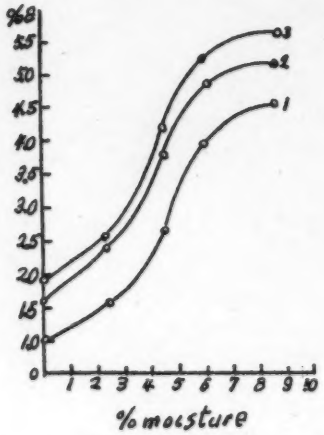

Fig. 15. Relation between the deformation of cotton cellulose, variety S-460. with the moisture, for different vegetation periods. 1) 35-Day cellulose; 2) 45-day cellulose; 3) 60 day cellulose.

The presence of moisture in fiber thus has a powerful effect on the deformation processes, and for this reason,

in describing the mechanical properties of cellulose materials, it is necessary to take account of the conditions under which they will be used. Here also may be put forward an hypothesis of a correlation between the character of the mechanical-properties curve of the fiber of different varieties and the rate of maturing of these varieties. In fact, the outstanding characteristic of the curve representing the change in strength of fiber, variety 3210, with age points to its rapidity of maturing.

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THE AUTOXIDATION OF ALLO-OCIMENE AND THE INTERMEDIATE PRODUCTS FORMED IN THE AUTOXIDATION PROCESS

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The autoxidation processes and intermediate products which have been most studied up to the present time are those dealing with the autoxidation of paraffin, cyclo-olefinic and aromatic hydrocarbons, and their derivatives [1]. On the other hand, the autoxidation processes and products of unsaturated aliphatic hydrocarbons have practically not been investigated at all up to now. Only in the case of the simplest olefins, for example, n-hexene, have detailed studies of the autoxidation products been made [2]. The more complicated olefinic hydrocarbons, including the dienes and trienes, which are of considerable practical interest, have not been subjected to detailed investigation, although the need for such investigation is very obvious.

In the course of work on the preparation of some derivatives of one of the aliphatic terpenes, allo-ocimene (2,6-dimethyloctatriene-2,4,6), we were impressed by the extreme ease of autoxidation of this hydrocarbon, and we resolved to study the process and the autoxidation products in greater detail. The marked tendency of allo-ocimene to autoxidize was first noted by B. A. Arbuzov [3], who established that the product formed had a composition closely corresponding to $C_{10}H_{16}O_2$, and gave a positive reaction for peroxides with potassium iodide.

Nikitin [4] studied the end-products obtained by the vacuum distillation of highly oxidized allo-ocimene, and he concluded that as a result of this treatment two products were formed: one was an unsaturated monohydric terpene alcohol (allo-ocimenyl alcohol), of composition $C_{10}H_{16}O$, obtained in a yield of about 50%, and the other consisted of a residue of solid polymer, the structure of which was not established. Apart from a small quantity of unreacted allo-ocimene and dipentene, present as impurity, no other products were observed. These studies contain the only information available on the autoxidation products of allo-ocimene. The mechanism of the process and the intermediate products have not been studied at all.

Allo-ocimene is a highly unsaturated aliphatic hydrocarbon with three conjugated double bonds in its molecule, which confer on it a high degree of chemical reactivity. There is no doubt that the extreme ease of oxidation of this hydrocarbon is determined by its highly unsaturated character, and the characteristic orientation of the double bonds in its molecule; these also have an influence on the direction of oxidation, and on the secondary reactions of the initially formed autoxidation products. The autoxidation of allo-ocimene shows considerable differences from the autoxidation of paraffins and simple alkene hydrocarbons, both in regard to the course of the reaction and to the primary and secondary products; this is proved in a conclusive manner by the experimental results given here.

The oxidation of allo-ocimene was effected in two ways: by allowing it to stand at room temperature for a time exposed to the air in vessels protected from dust, or by bubbling either air or pure oxygen through the liquid contained in tall, narrow vessels. The rate of absorption of oxygen at different stages in the autoxidation process was studied by means of the apparatus described by Zelinsky and Borisov [5].

Experiments showed that the allo-ocimene autoxidation process proceeds in a very characteristic manner, and several distinct stages in the process can be distinguished, not only by external criteria, but also by the chemical properties of the intermediates produced in the different stages. A study of the nature of these main intermediates and their interconversion, as well as the kinetics of the process, now enables us to draw some conclusions as to the nature of the allo-ocimene autoxidation process. These conclusions and observations may be of interest not only in the study of allo-ocimene, but also in the investigation of other aliphatic hydrocarbons having several conjugated double bonds.

In the present paper we shall describe the course of the allo-ocimene autoxidation process, and we shall give the chemical properties of the intermediates formed in the principal stages of this process.

In the first stage of the process, molecular oxygen vigorously combines with the allo-ocimene and extensive polymerization takes place. When one molecule of oxygen has been added to the allo-ocimene,

exposed in a thin layer, it is converted to an unstable polymeric peroxide compound—a polyperoxide of the composition $(C_{10}H_{16}O_2)n$, consisting of a spongy, elastic mass. After this vigorous absorption of one molecule of oxygen, further combination with oxygen and formation of polyperoxide is completely stopped for some time. Thus, the first stage in the autoxidation results in the formation of a polyperoxide, and this may be termed the oxidative-polymerization stage; it may be represented as follows:

$$\underset{\text{Allo-ocimene}}{nC_{10}H_{16}} + nO_2 \longrightarrow \underset{\text{Allo-ocimene polyperoxide}}{(C_{10}H_{16}O_2)n}$$

The peroxide nature of the main product of the first stage of autoxidation (the polyperoxide) is confirmed by the reaction of this product with potassium iodide, iodine being liberated, and also by its color reactions with guaiacum and with thiocyanate [1]. The polyperoxide does not react with lead tetraacetate and concentrated alkali solutions, which suggests that it does not contain appreciable quantities of hydroperoxide oxygen.

It is probable that the polyperoxide has a structure of the dialkyl peroxide type. It is poorly soluble in the usual organic solvents (and this property may be utilized in removing possible impurities), and is unsaturated: the degree of unsaturation was found to correspond to about two double bonds for each elementary molecule $C_{10}H_{16}O_2$. Because of its poor solubility and its instability, we were unable to determine its molecular weight.

The polyperoxide is very unstable, and decomposes on standing, or still more rapidly when slightly heated. When stored it lasts for only a few days. When sealed in ampoules without access of air, the polyperoxide is completely converted to a liquid in 7 to 10 days. This is the result of spontaneous depolymerization with the formation of the monomeric polyperoxide, $C_{10}H_{16}O_2$.

The slow conversion of the polyperoxide to the monomer is the second main stage in the allo-ocimene autoxidation process, and we term it the autodepolymerization stage. In this second stage there is no addition of oxygen. Only spontaneous depolymerization of the polyperoxide takes place. This was proved both by experiments in which the polyperoxide was stored in sealed ampoules, and also by a study of the oxygen absorption curves obtained when allo-ocimene was oxidized in the apparatus described above.

The polyperoxide depolymerization process proceeds at a rapid rate, and on heating to 60-70° for a short period it becomes strongly exothermic. The temperature then rises spontaneously to 165-175°, and the whole of the polyperoxide is converted to a liquid monomer having an elementary composition very close to that of the polyperoxide; this monomer is identical in chemical properties with the monomer formed by the slow spontaneous depolymerization of the polyperoxide.

The second main stage in the allo-ocimene autoxidation process may be represented as follows

$$\underset{\text{Polyperoxide}}{(C_{10}H_{16}O_2)n} \xrightarrow{\text{Autodepolymerization}} \underset{\text{Secondary oxide}}{nC_{10}H_{16}O_2}$$

Vacuum distillation of the products of both the spontaneous and thermal depolymerizations established that both these products consist of the same single monomeric component having the composition $C_{10}H_{16}O_2$; we term this the secondary oxide.

The purest sample of secondary oxide which we obtained was an almost colorless, mobile liquid with a characteristic odor, and having the following constants: b.p. 84-84.5° at 4 mm; n_D^{20} 1.4630-1.4635; d_4^{20} 0.951; M 168. The elementary composition was $C_{10}H_{16}O_2$, with one double bond.

Unlike the polyperoxide, the secondary oxide is not a peroxide compound, but, as our investigations showed, an aliphatic unsaturated terpene α-dioxide.

On hydration the secondary oxide forms the corresponding aliphatic unsaturated terpene tetrahydric alcohol—tetrite—in good yield; this has the composition $C_{10}H_{20}O_4$, and m.p. 124-125°.

Interaction of the secondary oxide with methanol in the presence of traces of sulfuric acid gave the dihydroxydimethyl ether, $C_{12}H_{24}O_4$, containing two hydroxyl and two methoxyl groups in the molecule (the constants of this ether are given in the experimental section).

When the secondary oxide was catalytically hydrogenated on a skeletonized nickel catalyst at ordinary pressure and room temperature, it took up 3 molecules of hydrogen per molecule to form a saturated aliphatic glycol of the terpene series, $C_{10}H_{22}O_2$ (the constants of this glycol are also given in the experimental section). These results provide sufficient confirmation that the secondary oxide is of the α-oxide type, and that it belongs to the aliphatic terpene series.

When the crude, undistilled products of the thermal or the spontaneous depolymerization of the poly-

peroxide were hydrated, we obtained in quite satisfactory yields a crystalline tetrite identical with the tetrite obtained by hydration of the pure secondary oxide. This is further proof that the secondary oxide is a normal product of the second stage in the autoxidation of allo-ocimene – the depolymerization stage – and is not formed during the vacuum distillation of the autoxidation products.

Therefore, the thermal and spontaneous depolymerization processes undergone by allo-ocimene polyperoxide are are essentially the same, the only difference being in the reaction rate.

The spontaneous depolymerization of allo-ocimene polyperoxide is an uncommon and very interesting example of the smooth decomposition of an organic peroxide compound to give an almost quantitative yield of dioxide.

If we assume that the polyperoxide has a dialkyl peroxide structure (and this is confirmed by experiment), then the polyperoxide depolymerization process must be considered as a complex of several simultaneous reactions: rupture of the oxygen-oxygen and the ethylene bonds of the polyperoxide with the subsequent closure of the free oxygen and carbon bonds formed to produce an α-oxide ring and a secondary oxide double bond.

The elucidation of the actual depolymerization mechanism depends on the precise determination of the position of the ethylene bond and the oxide rings in the secondary oxide molecule, and we shall presently consider these points. The formation of the secondary oxide concludes the second main stage in the allo-ocimene autoxidation process – the autodepolymerization stage.

In the third stage of the process more molecular oxygen is added to the secondary oxide. Since the secondary oxide is more saturated than the starting allo-ocimene, the rate of oxidation in this stage is several times slower than the rate in the first stage.

We did not succeed in separating any single compound from the products of the third autoxidation stage. These consist of a complex mixture of products, all at different stages of oxidation; and they include oxidation products of the secondary oxide and unreacted secondary oxide, the proportions depending on the length of the oxidation; the unreacted oxide can be separated by vacuum distillation. The residue obtained after distillation of the third stage products consists of a resinous product of variable composition, corresponding, on the average, to the general formula $C_{10}H_{16}O_3$.

From the results obtained, the allo-ocimene autoxidation process may be represented by the following main stages:

$$\underset{\text{Allo-ocimene}}{nC_{10}H_{16} + nO_2} \xrightarrow[\text{polymerization}]{\text{oxidation}} \underset{\text{Polyperoxide}}{(C_{10}H_{16}O_2)n} \xrightarrow{\text{autodepolymerization}} \underset{\text{Secondary oxide}}{nC_{10}H_{16}O_2}$$

EXPERIMENTAL*

Allo-ocimene was prepared by the thermal isomerization of α-pinene according to B. A. Arbuzov's method, [3]. Allo-ocimene with the following constants was used in the reaction: b.p. 81-82° at 12 mm; n_D^{20} 1.5430-1.5440; d_4^{20} 0.810-0.812.

Autoxidation of allo-ocimene

Experiment 1. Freshly distilled allo-ocimene was poured into flat beakers to form layers about 0.5 cm thick. The beakers were loosely covered with glass plates and allowed to stand in diffuse light. After 4 days nearly all the allo-ocimene was converted into a silvery, elastic mass of polyperoxide. An elementary analysis of this crude polyperoxide (the product was separated from a small amount of unoxidized allo-ocimene by squeezing between filter paper) gave the following results:

	Found %:	C 71.44; H 9.24.
$C_{10}H_{16}O_2$.	Calculated %:	C 71.42; H 9.53.

Experiment 2. Dry air was bubbled through a solution of freshly distilled allo-ocimene in ethanol (1:1) in a narrow vessel at room temperature. The bubbler consisted of a tube with a porous glass plate sealed on the end to provide a large contact surface between the allo-ocimene and the air. About three hours after the bubbling had commenced, white flakes of insoluble polyperoxide formed on the bottom of the cylinder. Heat was evolved slowly during the autoxidation process. From time to time the precipitated polyperoxide was removed from the bottom of the cylinder and fresh allo-ocimene was added.

The polyperoxide obtained in this way was washed with ethanol and dried to constant weight in a vacuum

* With the participation of E. A. Kalinovskaya and L. G. Konchevskaya.

desiccator at 30-35°. After drying, the polyperoxide consisted of an almost colorless elastic mass resembling rubber gelled in benzene. The elementary analysis of this polyperoxide was the same as that of the polyperoxide obtained in Experiment 1; both corresponded to the general formula : $C_{10}H_{16}O_2$.

Allo-ocimene polyperoxide is poorly soluble in such organic solvents as dioxane, acetone, ethyl acetate, diethyl ether, chloroform, petroleum ether , and benzene; and it is insoluble in methanol and ethanol. We made use of this property to separate it from allo-ocimene and other possible impurities. The polyperoxide was purified in the following manner: the crude material, obtained by either method, was carefully mixed in a beaker with five times as much ether to give a homogeneous, colloidal-like mass. Absolute ethanol was added to this mass to precipitate the polyperoxide, which separated as white flakes. After the solvent had been decanted, the polyperoxide was washed three times with ethanol and dried in vacuo at 30-35°. It was then obtained in the form of a colorless, elastic, rubber-like mass. Purification caused no material change in the elementary composition.

Investigation of the polyperoxide

1. Nature of the polyperoxide oxygen bonds

When the ethereal suspension of the polyperoxide (the ethyl ether must be freshly distilled) was shaken with aqueous potassium iodide solution, much iodine was liberated, and this reaction was evident even without the use of starch. The suspension also gave an intense blue color with guaiacum in the presence of ferric salts. Both of these reactions prove that the polyperoxide contains peroxide oxygen.

A very characteristic and sensitive reagent for peroxide compounds is the well-known thiocyanate, which consists of an aqueous acetone solution of ferric chloride and potassium thiocyanate. With the aid of this reagent it is possible to detect both organic hydroperoxides, and also the much less reactive dialkyl peroxides [1]. In a test tube 0.1 g of the polyperoxide and 4 ml of thiocyanate were placed. Immediately the original bright yellow reagent changed to dark red in the presence of the polyperoxide.

In order to establish the nature of the peroxide oxygen in the polyperoxide, reactions were carried out with lead tetra-acetate; these, as is known, are very characteristic for peroxide compounds containing hydroperoxide groups, and they proceed with the latter vigorously and with the spontaneous evolution of heat and oxygen [1]. It was found that the polyperoxide does not react with lead tetra-acetate, and from this it may be assumed that it does not contain notable quantities of hydroperoxide oxygen. It is probable that the polyperoxide has a dialkyl peroxide structure. However, this assumption needs further experimental proof, since, according to the method of Terentyev, the polyperoxide was found to contain 0.2% of active hydrogen, the nature of which we have not yet elucidated.

2. Determination of the degree of unsaturation of the polyperoxide

The determination was effected by titrating a weighed sample of polyperoxide in chloroform solution with benzoyl peroxide, according to the method of Nametkin and Bryusov [6]. 0.1926 g substance; 0.1826 g substance was added to 15 ml of benzoyl hydroperoxide solution. After two days, a back titration showed that 18.7 ml; 19.9 ml had been consumed. Found for $C_{10}H_{16}O_2$. 1.35, 1.37

Titration with benzoyl peroxide or hydroperoxides of other acids cannot be considered an accurate method for the determination of unsaturation in a polyperoxide, since the possibility that a further quantity of iodine might be separated, due to the action of the polyperoxide itself, in the process of titration of the excess benzoyl hydroperoxide, cannot be excluded.

The result obtained may be low compared with the true value, the number of double bonds being less. However, since other known methods (bromination, iodination) were found to be entirely unsuitable in our case, we decided to use this method. Bearing all that has been said above in mind, it can definitely be stated that the polyperoxide contains not less than two double bonds per elementary molecule $C_{10}H_{16}O_2$.

3. Behavior of the polyperoxide on storage without access of air (autodepolymerization of the polyperoxide

About 10 to 15 g of the polyperoxide was sieved into a small glass ampoule, air being excluded, and the ampoule was then stored in the dark at room temperature, and examined from time to time to find if the external appearance of the contents had changed. After 2 to 4 days, a gradual liquefaction of the original elastic polyperoxide mass was observed, and after 7 to 8 days the contents of the ampoule had become entirely converted to a mobile, yellow liquid (product of spontaneous depolymerization) with n_D^{20} 1.4850-1.4890. On opening the ampoule, neither diminution or increase of pressure was observed; this confirms that the process of spontaneous depolymerization proceeds without further addition or removal of oxygen. One of the ampoules was opened after 6 months, and the contents were identical with, and had the same constants, as those found

after 7 to 8 days.

The depolymerization product, unlike the peroxide, did not give the reactions described above, and was notable for its high sensitivity to acids. The addition of a drop of decinormal mineral acid, or the acid salt of a mineral acid dissolved in water, produced an immediate reaction in which resinification took place with evolution of heat. Anhydrous acid salts and organic acids had no action on the depolymerization product in the cold.

The depolymerization product takes part in reactions characteristic of α-oxides; it reacts in the cold with concentrated aqueous ethanolic solution of manganese chloride, manganese hydroxide being separated with the formation of an oil containing chlorine, and it also gives a brown coloration with an ethanolic solution of pyridine.

On distillation under reduced pressure, the depolymerization product was obtained in the main fraction with b.p. 82 to 84° at 4 mm; n_D^{20} 1.4645, 1.4650; and d_4^{20} 0.951, 0.952, having the composition $C_{10}H_{16}O_2$.

4. Behavior of the polyperoxide on heating (thermal depolymerization of the polyperoxide)

10 g of the purified polyperoxide was placed in a round-bottomed flask connected to a reflux condenser. Inside the flask a thermometer was fixed so that the mercury bulb was immersed in the polyperoxide. The flask was slowly heated on a water bath from 20°. When the temperature of the bath had reached 65°, the polyperoxide began to melt with vigorous decomposition, and the evolution of a large amount of heat, which resulted in a rise in temperature within the flask to 170° (spontaneous). The vigorous decomposition reaction continued for a minute. There was no marked change in the weight of the flask before and after the reaction. As a result of the reaction the polyperoxide was converted into a mobile, bright yellow liquid (with the constants: n_D^{20} 1.4740; d_4^{20} 0.944).

	Found %:	C 70.6, 70.71; H 9.6, 9.62
$C_{10}H_{16}O_2$.	Calculated %:	C 71.42; H 9.53.

The thermal depolymerization product, like the autodepolymerization product, reacts vigorously with mineral acids and with aqueous solutions of acid salts in the cold. It resinified with spontaneous evolution of heat; it did not give the qualitative reactions for peroxide; it reacted with manganese chloride, and gave a coloration with pyridine.

On distillation under reduced pressure, the thermal depolymerization product was obtained in the main fraction with b.p. 82-84° at 4 mm; n_D^{20} 1.4650, and d_4^{20} 0.951. The fraction had the elementary composition $C_{10}H_{16}O_2$. The chemical properties of the fraction were entirely analogous to the properties of the fraction obtained when the spontaneous autodepolymerization product of the polyperoxide was distilled.

Further experiments showed that the spontaneous and thermal depolymerization products consisted of one and the same compound, which we have termed the secondary oxide. These depolymerization products and the main fractions obtained by their distillation under reduced pressure did not differ in elementary composition or in chemical properties, and they were also very similar in their physical constants. From this it may be concluded that both the spontaneous and the thermal depolymerization of the polyperoxide are similar to one another.

Investigation of the polyperoxide depolymerization product (secondary oxide)

1. Preparation of pure secondary oxide

The impurities in the secondary oxide may include a small quantity of unreacted allo-ocimene, and also isomerization products of the secondary oxide itself containing carbonyl groups. The secondary oxide was easily purified by repeated distillation in vacuum, and therefore its purification presented no special difficulties.

The purest samples of secondary oxide, which we obtained by double distillation under reduced pressure with a column containing glass rings and having an efficiency of 15 theoretical plates, used in our study had the following constants: b.p. 84 to 84.5° at 4 mm; n_D^{20} 1.4630-1.4635; d_4^{20} 0.951; M 168, (cryoscopic in benzene solution). Elementary composition (repeated determinations) $C_{10}H_{16}O_2$.

2. Determination of degree of unsaturation of the secondary oxide

The determination was effected by two methods: titration with benzoyl hydroperoxide according to Nametkin and Bryusov [6], and bromination by the method of MacIlliney with modifications by Virbyants and Meshcheryakova[7]. The results of both methods agreed. It was found that the molecule of the secondary oxide contains one ethylene bond.

3. Determination of the nature of the oxygen-carbon bonds in the secondary oxide

Determination of active hydrogen. Active hydrogen was determined by the method of Terentyev and Kireev [8] with the aid of Chugaev's reagent. It was found that the secondary oxide contains no active hydrogen.

Determination of peroxide oxygen. The freshly distilled secondary oxide did not liberate iodine from aqueous solutions of potassium iodide and did not give a color reaction with thiocyanate or with resin. Therefore it contains neither peroxide nor hydroperoxide oxygen.

Reaction of the α-oxide oxygen

Color reaction with pyridine. A drop of the secondary oxide was dissolved in ethanolic pyridine mixture (1:5). After 15 hours the original colorless, clear solution assumed a bright brown, and after 7 days a dark brown color, characteristic of α-oxide. Zimakov [9] points out that this is a very sensitive and specific test for α-oxides.

Interaction of the secondary oxide with manganese chloride. It is known that the similarity of α-oxides to the hydrohalogen acids is so great that they may decompose some salts of these acids with the formation of metal hydroxides [10]. It was found that our secondary oxide reacted very well with manganese chloride even in the cold. 3.3 g of secondary oxide was mixed in solution with 12 g of manganese chloride (crystalline hydrate) and 12 ml of ethanol in a test tube with a ground glass stopper. At the same time a blank experiment was carried out. After a day the tube with the oxide showed a copious precipitate of manganese hydroxide, and on the surface a layer of oil formed. The blank tube was unchanged. The hydroxide was filtered off, washed with ethanol, and dried to constant weight. 1.61 g of hydroxide was obtained. The filtrate was diluted with water and extracted with ether. The ethereal extract was washed with water and dried over calcium chloride. After the ether had been removed on the water-bath under reduced pressure, 1.53 g of a yellow oil with an agreeable fruity odor (n_D^{20} 1.4802) was obtained. The quantitative determination of chlorine in this oil carried out according to Stepanov gave the following results:

Found %: Cl 24.0

$C_{10}H_{17}O_2Cl$. Calculated %: Cl 17.4

$C_{10}H_{18}O_2Cl_2$. Calculated %: Cl 29.45

Consequently, the product of the interaction of secondary oxide with manganese chloride is dichlorohydrin mixed with unreacted secondary oxide.

Quantitative determination of α-oxide oxygen

The quantitative determination of α-oxide oxygen was effected by the method of Nikolya and Polter, described by Nazarov and Akhrem [11]. The method consists of rupturing the α-oxide rings with 0.2 N solution of dry hydrogen chloride in absolute ether. Nazarov and Akhrem successfully applied this method to the determination of α-oxide oxygen in keto dioxides, and they noted that the reaction of fission of the oxide rings proceeds slowly, requiring about 14 days. Our oxide was found to behave similarly. After 12 days we found in the secondary oxide only 1.03 oxide rings. Considerable increase in the length of the experiment led to no material change in the results.

Interaction of the secondary oxide with methanol

Since it was observed that the secondary oxide had α-oxide properties, we decided to make a further study of these properties. It is known that α-oxides can react with alcohols to form the corresponding monoalkyl ethers. The action is catalyzed by various acid reagents [9]. 28.1 g of secondary oxide dissolved in 60 ml of absolute methanol was gradually added to 60 ml of methanol containing 0.3 g of sulfuric acid, care being taken that the temperature did not exceed 40-45°. The reaction mixture was neutralized with the calculated amount of sodium methoxide. After removal of the excess alcohol and drying in vacuum, 38.4 g of reaction product was obtained. (If we assume that the secondary oxide contains two α-oxide rings, then the theoretical yield of the ether should amount to 38.8 g. Therefore, the actual yield of crude product amounts to 97.5% of theory.)

Distillation of 31.2 g of this crude product under reduced pressure in a Claisen flask gave 22.5 g of a fraction with b.p. 141-142° at 10 mm; n_D^{20} 1.4670; d_4^{20} 1.017. This was almost pure dihydroxydimethyl ether: M (Rast) in camphor 225; calculated, 232.

Found %: C 62.64; H 10.37.

$C_{10}H_{16}(OH)_2(CH_3O)_2$. Calculated %: C 62.07; H 10.33

By bromination one ethylene bond was found. A Zeisel determination showed 23.7, 23.9% of CH_3O. Two OH groups were found in the molecule by Terentyev's method, $C_{10}H_{16}(OH)_2(CH_3O)_2$. If the molecule of the addition product of methanol to the secondary oxide has two methoxide and two hydroxyl groups, it must be

assumed that the initial secondary oxide is a dioxide.

Hydrogenation of the secondary oxide

Hydrogenation was carried out at room temperature under atmospheric pressure, an skeletonized nickel catalyst being used; this was prepared by the usual method of treating a nickel aluminum alloy with alkali.

In the experiment 20.1 g of secondary oxide, 50 ml of ethanol (as solvent) and a catalyst prepared from 35 g of nickel-aluminum alloy were used. (Capacity 200 ml; number of vibrations 184 per minute). The hydrogenation proceeded very smoothly at the rate of 120 ml per minute. A total of 8,100 ml of H_2 was absorbed. In theory, if we consider that the secondary oxide molecule has one ethylene bond and two α-oxide rings, 8,753 ml should be absorbed. Therefore, 2.78 moles of H_2 were added per mole of oxide. The catalyst was filtered off, the ethanol removed by distillation, and the hydrogenation product distilled under reduced pressure from a Claisen flask. 16.6 g of product was distilled. 13 g of a fraction which completely came over between 130 and 131° at 10 mm; n_D^{20} 1.4560; d_4^{20} 0.933, was obtained.

	Found %:	C 69.0, 69.0; H 12.2; 12.12
$C_{10}H_{20}(OH)_2$	Calculated %:	C 69.0; H 12.65

This had no ethylene bonds. By Terentyev's method, two OH groups were found. Consequently, the main product of the addition of three moles of hydrogen to one mole of a secondary oxide is a saturated aliphatic terpene glycol of composition $C_{10}H_{20}(OH)_2$. This confirms that the secondary oxide itself is a terpene dioxide of the aliphatic series.

Hydration of the secondary oxide

37.7 g of secondary oxide was gradually added to 150 ml of decinormal aqueous sulfuric acid with vigorous stirring, care being taken to see that the temperature of the reaction mass did not exceed 35° (water cooling). The reaction mixture – a cloudy, bright-yellow liquid – was extracted four times with toluene. The last extract was entirely clear and colorless. The aqueous layer after the extraction, consisting of a clear, colorless liquid, was neutralized with 6 g of barium carbonate. After a day the precipitated sulfur and excess barium carbonate were filtered off. The filtrate was concentrated under reduced pressure (25 mm) at 50°, and the residue was dried in vacuum to constant weight.

43.15 g of hydration product was obtained. If the secondary oxide molecule contains two α-oxide rings, then the theoretical amount of hydration product should be 45.7 g. Therefore, the yield amounts to 94.5% of theory.

The hydration product was a thick, resinous mass of a bright-yellow color, odorless, and with a bittersweet taste. On long storage (1.5 months) it gradually crystallized, forming a mass resembling crystallized honey. It was easily soluble in water and in alcohols. It was insoluble in diethyl ether, chloroform, and in benzene. After two recrystallizations from acetone and drying at 105°, a crystalline product with m.p. 124-125° was obtained in good yield; this resembled granulated sugar. Analysis of this crystalline product gave the following results:

	Found %:	C 58.72, 58.6; H 9.53, 9.64
$(C_{10}H_{16}(OH)_4$	Calculated %:	C 58.82; H 9.80

Molecular weight (Rast, in camphor) 198; calculated M for $C_{10}H_{16}(OH)_4$ 204; found (Terentyev) OH groups, %: 31.2, 30.4; calculated % OH groups 33.3.

The crystalline hydration product contained one ethylene bond. Heating with acetic anhydride in the presence of anhydrous sodium acetate resulted in acetylation of only two hydroxide groups. The second two hydroxide groups did not acetylate under these conditions, but remained free. The hydration experiments were repeated several times with the same results. Thus, the experiments showed that the main hydration product of the secondary oxide is an unsaturated aliphatic tetrahydric terpene alcohol – tetrite – of composition $C_{10}H_{16}(OH)_4$. From this it must also be assumed that the secondary oxide is an aliphatic terpene α-dioxide.

SUMMARY

1. The course of the allo-ocimene (2,6-dimethyloctatriene-2,4,6) autoxidation has been studied. It has been found that the process proceeds in stages. The composition and properties of the intermediate products for the individual stages of the process have been described.

2. The chemical properties of a secondary oxide – the main intermediate product of the second autoxidation stage – have been studied. It was found to be an aliphatic terpene dioxide.

3. For the first time new aliphatic terpene derivatives have been obtained from the secondary oxide: an unsaturated tetrite, a saturated glycol, and a dihydroxy dimethyl ether.

4. A mechanism is proposed for the allo-ocimene oxidation process.

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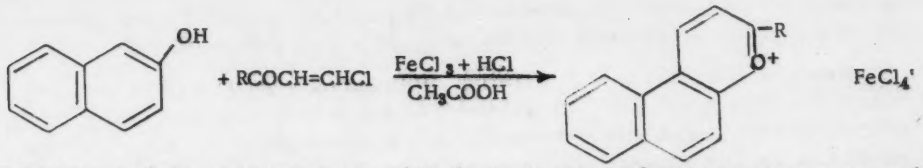
THE SYNTHESIS OF 2-ALKYLNAPHTHO- and 2-ALKYLBENZOPYRANYL SALTS FROM β-CHLOROVINYLKETONES

A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya

In one of our previous papers [1], it was shown that when methyl-β-chlorovinylketone and β-naphthol are allowed to interact in the presence of anhydrous ferric chloride and concentrated hydrochloric acid in acetic acid solution, a high yield of 2-methylnaphthopyranyl ferrichloride is obtained. Further studies showed that this reaction is quite general; under the same conditions, homologs of methyl-β-chlorovinylketone afford 2-alkylnaphthopyranyl ferrichlorides:

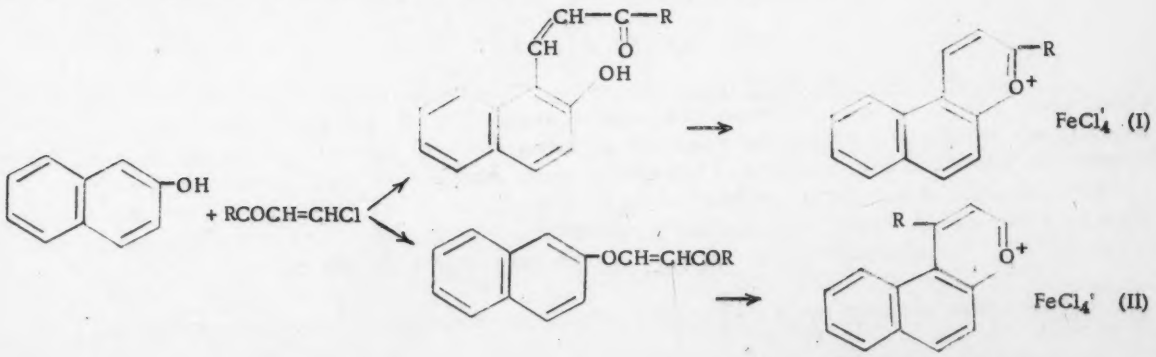


For the success of the reaction the purity of the ferric chloride is of great importance: we used anhydrous sublimed ferric chloride. With this the ferrichloride yields varied from 50 to 90%, depending on the nature of the radical in the alkyl-β-chlorovinylketone. When commercial hydrated ferric chloride was used, the reaction did not go in the required direction.

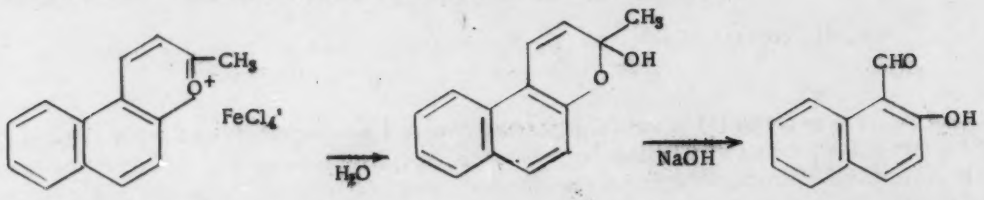
We attempted to prepare naphthopyranyl salts from β-naphthol and alkyl-β-chlorovinylketones, using other acid condensing agents. In the presence of perchloric acid no pyranyl salts were formed, but instead we obtained a colorless crystalline substance having m.p 230°, the structure of which we have not yet established. Condensation in the presence of sulfuric acid gave very small amounts of pyranyl salts, and this procedure did not seem likely to have any advantages.

The first homolog in the series of naphthopyranyl salts which we prepared, 2-methylnaphthopyranyl chloride, has recently [2] been prepared by the condensation of β-naphthol with methylethinylketone in the presence of ferric chloride. For this compound the authors give m.p. 141-143°; absolutely pure 2-methylnaphthopyranyl ferrichloride actually melts at 151-152°. The method we developed for the synthesis of alkylnaphthopyranyl salts has an advantage over the method of preparing them from alkylethinylketones: the starting materials, the alkyl-β-chlorovinylketones, are readily accessible, whereas the ethinylketones, especially the alkylethinylketones, are fairly difficult to obtain. The alkylnaphthopyranyl ferrichlorides obtained are red crystalline substances; they crystallize well from glacial acetic acid, and are soluble with difficulty in most organic solvents. When heated with hydroxylic solvents, they undergo changes apparently connected with the opening of the pyran ring. The color of the products varies from green to red, depending on the alkyl radical.

When β-naphthol reacts with alkyl-β-chlorovinyl ketone, the formation of two isomeric alkylnaphthopyranyl salts is theoretically possible, according to the following reactions (I) and (II)

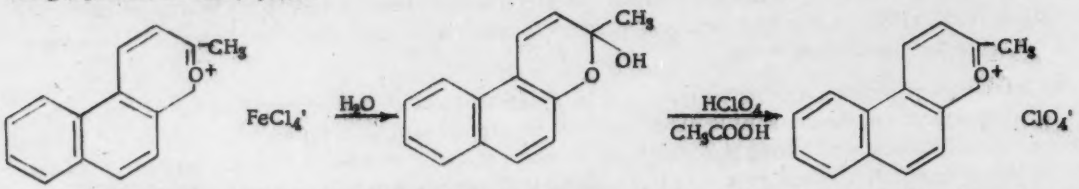


Up to now it has not been possible to exclude the second of these reactions, since we have previously shown [1] that alkyl-β-chlorovinylketones react with phenols to form β-aroxyvinylketones, and the cyclization of these under the reaction conditions could lead to the formation of the isomeric 4-alkylnaphthopyranyl ferrichlorides. In all cases we obtained only one compound from the reaction mixture. We proved the structure of the compounds obtained, using the first homolog as an example, by degradation. When the ferrichloride is treated with aqueous sodium acetate the pseudobase is formed, and when this is treated with alkali, it undergoes hydrolytic cleavage at the carbon-carbon double bond, as is usual for compounds of this type [3]; as a result 2-hydroxynaphthaldehyde-1 is formed, and we separated this from the reaction mixture:

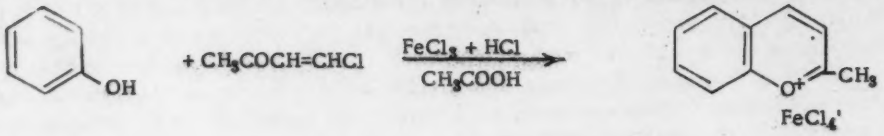


Therefore, for the compounds obtained, the 4-alkylnaphthopyranyl salt structure which should yield 1-acylnaphthol-2 on hydrolytic cleavage may be excluded. It should be mentioned that direct treatment of the pyranyl salt with alkali or ammonia, as is usually recommended for the benzopyranyl salts [3], in our case leads only to the formation of the crystalline substance with m.p. 230° which has already been mentioned.

The alkylnaphthopyranyl ferrichlorides obtained may be used as starting materials for the preparation of naphthopyranyl salts containing other anions. We prepared 2-methylnaphthopyranyl perchlorate from the corresponding ferrichloride; this was treated with an aqueous solution of sodium acetate and the ethereal solution of the resulting pseudo-base was then allowed to react with a mixture of acetic and perchloric acids, the perchlorate being separated in 52.9% yield:



The synthesis we have worked out for pyranyl salts may also be used for the preparation of benzopyranyl salts. Using phenol as an example, we showed that hydroxy derivatives of the benzene series also react with β-chlorovinylketones in the presence of ferric chloride and concentrated hydrochloric acid to form benzopyranyl salts:



Here the yield of pyranyl salt is much lower (15%); however, the reaction is mainly of interest because it shows the wide possibilities of synthesizing pyranyl salts from β-chlorovinylketones. The methylbenzopyranyl salt which separated had its methyl radical in position 2; we showed this by comparing the reaction product with the substance obtained by the known method [4] from methyl-o-hydroxycinnamylketone. The structure of alkylbenzopyranyl salts prepared from alkyl-β-chlorovinylketone is therefore similar to that of the alkylnaphthopyranyl salts obtained by the same method.

EXPERIMENTAL

1. Preparation of 2-methylnaphthopyranyl ferrichloride. To a solution of 0.5 g of β-naphthol in 5.0 ml of glacial acetic acid were added 0.5 g of methyl-β-chlorovinylketone and 5.0 ml of a solution of anhydrous ferric chloride in concentrated hydrochloric acid (the solution was prepared with the following proportions: 10.0 g of ferric chloride to 15.0 ml of concentrated hydrochloric acid). After an hour, the precipitate which had separated was collected and washed with a small quantity of glacial acetic acid, and then with absolute ether. Yield 1.0 g (74% of theoretical). After repeated recrystallization from glacial acetic acid, the 2-methylnaphthopyranyl ferrichloride was obtained as dark-green, acicular crystals with m.p. 151-152°*

* In a previous paper a m.p. of 146° was given. It was found that after repeated recrystallization the m.p. rose to 152°.

Found %: C 42.85, 42.67; H 3.02, 2.98.

$C_{14}H_{11}OCl_4Fe$. Calculated %: C 42.75; H 2.82.

The compound dissolved readily in hot acetic acid, but was insoluble in benzene and in ether; it was decomposed by water.

II. Degradation of 2-methylnaphthopyranyl ferrichloride. Two grams of finely ground 2-methylnaphthopyranyl ferrichloride was mixed with 50.0 ml of water and 20.0 ml of saturated sodium acetate solution. The pseudobase which separated was extracted with ether. The ether was distilled off and 20% sodium hydroxide solution was added to the residue. The orange solution was boiled under reflux until nearly all the color had disappeared. 20% sulfuric acid was then added to the filtered solution. The precipitated 2-hydroxynaphthaldehyde-1 was collected on a filter and dried over calcium chloride in a vacuum desiccator; the m.p. was 80°. The literature [5] gives m.p. 81°.

The oxime of the aldehyde had m.p. 156°; the literature [6] gives 157°.

III. 2-Methylnaphthopyranyl perchlorate. 1.7 g of finely ground 2-methylnaphthopyranyl ferrichloride, prepared by Method I, was mixed with 70.0 ml water. To the mixture 20.0 ml of saturated sodium acetate solution was added. The reaction mixture was vigorously shaken. The pseudobase which separated was extracted with ether. To the ethereal extract 10.0 ml of glacial acetic acid was added, and the ether was removed by distillation. To the residue 10.0 ml of 70% perchloric acid was added. The contents of the flask were heated until all the residue had dissolved, after which the flask was allowed to stand overnight. 2-Methylnaphthopyranyl perchlorate separated in the form of dark-green crystals. Yield 0.7 g (52.9% of theoretical). After recrystallization from glacial acetic acid, the m.p. was 179-180°.

Found %: C 56.71, 56.85; H 3.53, 3.54.

$C_{14}H_{11}O_5Cl$. Calculated %: C 57.06; H 3.76.

The compound was readily soluble in glacial acetic acid, but insoluble in benzene and in ether; it was decomposed by water.

IV. 2-n-Propylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 1.6 g of n-propyl-β-chlorovinylketone, 2.0 g of β-naphthol, and 12.0 ml ferric chloride in concentrated hydrochloric acid, the whole being mixed in 20.0 ml of glacial acetic acid. Yield 5.5 g (93% of theoretical). After recrystallization from glacial acetic acid, 2-n-propylnaphthopyranyl ferrichloride was obtained as bright-green crystals with m.p. 124°.

Found %: C 45.48, 45.56; H 3.66, 3.59; Fe 13.23, 13.43.

$C_{16}H_{15}OCl_4Fe$. Calculated %: C 45.62; H 3.58; Fe 13.27.

V. 2-Isopropylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 10 g of isopropyl-β-chlorovinylketone, 1.2 g of β-naphthol, and 6.5 ml of solution of ferric chloride in concentrated hydrochloric acid, the whole in 15.0 ml of glacial acetic acid. Yield 2.5 g (71.4% of theoretical). After recrystallization from glacial acetic acid, 2-isopropylnaphthopyranyl ferrichloride was obtained as yellow acicular crystals. The compound melted at 100.5°, then solidified as the temperature was further raised and melted again at 157°.

Found %: C 45.78, 45.66; H 3.76, 3.66; Fe 13.22, 13.23.

$C_{16}H_{15}OCl_4$. Calculated %: C 45.62; H 3.58; Fe 13.27.

VI. 2-Isobutylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 1.1 g of isobutyl-β-chlorovinylketone, 1.0 g of β-naphthol, and 6.0 ml of solution of ferric chloride in concentrated hydrochloric acid, the whole in 10 ml of glacial acetic acid. Yield 2.2 g (73% of theoretical). After repeated recrystallization, 2-isobutylnaphthopyranyl ferrichloride was obtained as brilliant yellow platelets with m.p. 103°.

Found %: C 47.05, 46.96; H 3.68, 3.77; Cl 32.48, 32.65; Fe 12.62, 12.57.

$C_{17}H_{17}OCl_4Fe$. Calculated %: C 46.89; H 3.91; Cl 32.64; Fe 12.87.

VII. 2-n-Amylnaphthopyranyl ferrichloride. This was prepared as in Experiment I from 4.0 g of amyl-β-chlorovinylketone, 3.5 g of β-naphthol, and 20.0 ml of hydrochloric acid solution of ferric chloride, the whole in 30.0 ml of glacial acetic acid. Yield 5.0 g (50% of theoretical). After repeated recrystallization, 2-n-amylnaphthopyranyl ferrichloride was obtained as reddish-brown plates with m.p. 74°.

Found %: C 48.14, 48.18; H 4.42, 4.37; Cl 31.62, 31.65; Fe 12.22, 12.31.

$C_{18}H_{19}OCl_4Fe$. Calculated %: C 48.16; H 4.27; Cl 31.58; Fe 12.44.

VIII. 1-Methylbenzopyranyl ferrichloride. This was prepared as in Experiment I from 8.0 g of methyl-β-chlorovinylketone, 8.0 g of phenol, and 30.0 ml of hydrochloric acid solution of ferric chloride, the whole in

48.0 ml of glacial acetic acid. The precipitate was obtained after 5 hours. Yield 4.0 g (15% of theoretical). After recrystallization from glacial acetic acid, 2-methylbenzopyranyl ferrichloride was obtained as bilberry-red crystals with m.p. 125°. The literature [4] gives 118°.

IX. Synthesis of 2-methylbenzopyranyl ferrichloride by Decker's method. To a solution of 1.0 g of methyl-o-hydroxycinnamylketone [7] in 10.0 ml of glacial acetic acid, 10 ml of solution of anhydrous ferric chloride in concentrated hydrochloric acid was added. The reaction mixture was heated to boiling and allowed to stand overnight. The crystals which separated were filtered off and several times recrystallized from glacial acetic acid. Bilberry-red crystals were obtained with m.p. 124°; the literature [4] gives m.p. 118°.

SUMMARY

1. A new method of preparing 2-alkylnaphthopyranyl salts from the easily accessible alkyl-β-chlorovinylketones is described. The method makes it possible to prepare 2-alkylnaphthopyranyl salts in good yield.

2. It is shown that it is possible to convert the ferrichlorides obtained into the corresponding alkylnaphthylpyranyl perchlorates.

3. When the 2-methylnaphthopyranyls were treated with alkali, 2-hydroxynaphthaldehyde-1 was obtained; this proves the structure of the naphthopyranyl salts.

4. It is shown that phenol also reacts with methyl-β-chlorovinylketone to form 2-methylbenzopyranyl salts.

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THE ACTION OF PHOSPHORUS TRICHLORIDE ON THE ETHYL ESTERS OF ORTHOPROPIONIC AND ORTHOSILICIC ACIDS

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In Post's monograph "The Chemistry of the Aliphatic Orthoesters" [1], the results obtained by Bassett [2] on the action of phosphorus trichloride on orthoformic acid are given; this results – according to Bassett – in the formation of monoethyl phosphite; according to Arnold [3], whose results are also given, triethyl phosphitie is formed in this reaction:

$$3HC(OC_2H_5)_3 + PCl_3 \longrightarrow 3HCOOC_2H_5 + 3C_2H_5Cl + (C_2H_5O)_3P.$$

Examination of Arnold's paper shows that when phosphorus trichloride and orthoformic ester are reacted in equimolecular proportions ethyl chloride is evolved. From the reaction products Arnold separated a fraction boiling at 55-75° which, according to him, consisted of ethyl formate and phosphorus trichloride, and a fraction boiling at 150-190°, which he considered to be triethyl phosphite. Arnold gave no data to confirm the formation of triethyl phosphite. The same monograph describes Friedel and Ladenburg's [4] preparation of ethyl phosphite and ethyltrichlorosilane by the interaction of phosphorus trichloride and ethyl silicopropionate.

On consulting the actual paper of Friedel and Ladenberg, it was found that they only expected to obtain triethyl phosphite and ethyltrichlorosilane, but on carrying out the reaction with ethyl silicopropionate, they obtained a fraction boiling at 110-150°; but they did not succeed in separating a constant-boiling fraction from this.

In order to find if it were possible to obtain esters of phosphorous acid by reacting phosphorous trichloride and orthoesters, we reacted phosphorous trichloride with the ethyl esters of orthopropionic and orthosilicic acids. On reacting orthopropionic ester with phosphorus trichloride in equimolecular proportions (Arnold's conditions) we obtained a fraction corresponding to the chloranhydride of Menshutkin. This reaction was in accordance with the equation:

$$CH_3CH_2-C(OC_2H_5)_3 + PCl_3 = CH_3CH_2-COOC_2H_5 + C_2H_5Cl + C_2H_5OPCl_2$$

When the reagents were in the proportion of 2 moles of orthopropionic ester to 1 mole of phosphorus trichloride, a fraction was separated the constants and analysis of which corresponded to the chloranhydride of diethylphosphorous acid:

$$2CH_3CH_2-C(OC_2H_5)_3 + PCl_3 = 2CH_3CH_2-COOC_2H_5 + 2C_2H_5Cl + (C_2H_5O)_2PCl.$$

With a ratio of 3 moles of orthoester to 1 mole of phosphorus trichloride, as we have shown, triethyl phosphite is formed:

$$3CH_3CH_2-C(OC_2H_5)_3 + PCl_3 = 3CH_3CH_2-COOC_2H_5 + 3C_2H_5Cl + P(OC_2H_5)_3,$$

and this was proved by the constants of the phosphorous ester and by the formation with CuI of a complex crystalline compound, $CuI \cdot P(OC_2H_5)_3$ with m.p. 109-110° [5]. In the latter case, in addition to triethyl phosphite, a substance with the following constants was separated: b.p. 140-142° at 14 mm; d_{20}^{20} 1.0353; n_D^{20} 1.4324. The analysis and properties of this compound corresponded to the ethyl ester of the acetal of propionylphosphinic acid:

$$CH_3CH_2-C(OC_2H_5)_2-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$$

In order to prove the structure of this compound, propionylphosphinic acid ester was prepared by the action of propionyl chloride on triethyl phosphite:

$$CH_3CH_2COCl + P(OC_2H_5)_3 = CH_3CH_2COP(OC_2H_5)_2 + C_2H_5Cl$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

with the following constants: b.p. 100.5-102.5° at 8 mm; d_{20}^{20} 1.0893; n_D^{20} 1.4230. The semicarbazone had m.p. 160-162°.

An attempt was made to obtain the acetal of propionylphosphinic ester by the action of orthoformic ester [6], but the results were negative. Then the substance with b.p. 140-142° at 14 mm, obtained by the interaction of orthopropionic ester and phosphorus trichloride, was carefully saponified in the cold. The saponification product gave a semicarbazone with m.p. 162-163°. These results show that the compound with b.p. 140-142° at 14 mm is the diethyl acetal of propionylphosphinic acid ester.

The formation of the acetal of propionylphosphinic acid ester may be considered as taking place in the following way: orthopropionic ester first reacts with phosphorus trichloride to form the chloro-ether according to the following equation:

$$CH_3CH_2-C(OC_2H_5)_3 + PCl_3 = CH_3CH_2C(OC_2H_5)_2 + C_2H_5OPCl_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Cl$$

The chloro-ether reacts with the triethyl phosphite formed, giving the ester of propionylphosphinic acid acetal:

$$CH_3CH_2-C(OC_2H_5)_2 + P(OC_2H_5)_3 = CH_3CH_2-C(OC_2H_5)_2 + C_2H_5Cl$$
$$\qquad\qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad Cl \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O=P(-OC_2H_5)_2$$

The possibility that the chloro-ether might be formed as an intermediate has already been mentioned by Arnold [3].

The reaction of phosphorus trichloride with ethyl orthosilicate did not yield such a clear picture. The best results were obtained with a ratio of 3 moles of orthosilicic ester to 4 of phosphorus trichloride. But even with this ratio, the only substance separated in the pure state was triethoxymonochlorosilane. Fractions were also obtained corresponding to Menshutkin's chloranhydride and to diethoxydichlorosilane, contaminated with products containing phosphorus. Triethylphosphite was not obtained.

EXPERIMENTAL

Reaction of 3 molecules of orthopropionic ethyl ester with 1 molecule of phosphorus trichloride

To 40 g of ethyl orthopropionic ester (b.p. 60° at 17 mm) 10.6 g of phosphorus trichloride was added. The mixture boiled up vigorously and the temperature rose to 70°. At first a white precipitate was formed, but as the trichloride was added, a colorless liquid formed. When all the trichloride had been added, the reaction mixture was heated for 2 hours on the water-bath. Distillation with a Widmer column afforded the following fractions:

Fraction I, with b.p. 22-25° at 16 mm (at atmospheric pressure it distilled at 98.5-99.5°); d_{20}^{20} 0.8938; $n_D^{20.1}$ 1.3860; yield 10.1 g. Corresponds to the ethyl ester of propionic acid.

Fraction II b.p. 52 to 55° at 13 mm; d_{20}^{20} 0.9677; n_D^{20} 1.4101; yield 9.8 g. Corresponds to triethyl phosphite. Proved by the formation of the complex $CuI \cdot P(OC_2H_5)_3$, with m.p. 109-110° [5].

Fraction III, with b.p. 140-142° at 14 mm; d_{20}^{20} 1.0353; n_D^{20} 1.4324; yield 9.9 g. Corresponds to the diethyl acetyl of the ethyl ester of propionyl phosphinic acid.

Analysis of fraction III.

Found %: C 49.30; H 9.51; P 11.83 (Neiman); 11.87 (amperometric)

$C_{11}H_{25}O_5P$. Calculated %: C 49.25; H 9.3; P 11.6.

Saponification of Fraction III. To 1 g of the substance 1 ml of distilled water and 3 drops of concentrated HCl were added. The flask was closed with a cork and set aside. For the first three days the liquid layers did not mix. After standing for two weeks at room temperature the liquid became completely homogeneous. The water was distilled off under reduced pressure and the residue distilled at a temperature of 108-110° at 12 mm; n_D^{20} 1.4265; yield 0.4 g.

Preparation of the semicarbazone. To 0.2 g of the saponified product, 0.3 g of sodium acetate was added, together with a small quantity of absolute ethanol. To this solution an aqueous solution of 0.3 g of semicarbazide

hydrochloride was added and then sufficient ethanol to dissolve the crystals completely. It was then stirred with a glass rod and allowed to stand. After standing for two months, clear white crystals separated as tablets — the inorganic part. On concentrating the aqueous layer, a yellow oil at first easily separated, and then white crystals in the form of granules appeared; these were insoluble in water and had m.p. 160-163°. The yield was insignificant.

Preparation of the ethyl ester of propionylphosphinic acid. To 28 g of triethyl phosphite, 15.5 g of propionyl chloride, b.p. 80-85°, was added dropwise. The reaction was carried out in an Arbuzov flask. Each drop of propionyl chloride produced a sizzling and an increase in temperature. The thermometer placed at the joint of the Arbuzov flask showed a temperature of 40°. When all the propionyl chloride had been added, hydrogen chloride was sucked off in vacuum and the mixture was distilled. There was then obtained:

Fraction I, with b.p. up to 100° at 8 mm; 1.6 g.
Fraction II, with b.p. 100.5° to 102.5° at 8 mm; 14.5 g; d_{20}^{20} 1.0893; n_D^{20} 1.4230.
Fraction III, residue, 3.4 g.

The residue could not be distilled and consisted of a colorless solid mass easily soluble in water.

On repeated distillation of parts of Fraction II, no constant boiling product could be obtained; the temperature gradually rose from 67° at 8 mm to 121° at 8 mm and only 30% was obtained in the fraction with b.p. 100.5-102.5° at 8 mm having d_{20}^{20} 1.080; n_D^{20} 1.4201. Subsequent fractionations gave no fractions boiling within narrow temperature ranges.

Analysis of Fraction II for phosphorus

Found %: P 16.20, 16.27.
$C_7H_{15}O_4P$. Calculated %: P 15.98.

Reactions of the CO group with the ethyl ester of propionylphosphinic acid.

With nitroprusside of sodium. The product in small quantity was diluted with an equal volume of water, and a crystal of nitroprusside of sodium was added; to this solution was added 10% of sodium hydroxide solution. The solution became bright apple-green.

Preparation of the semicarbazone. In a test tube with the smallest possible quantity of water 0.65 g of semicarbazide hydrochloride was dissolved; in another tube 0.5 g of propionylphosphinic ester and 0.65 g of sodium acetate were placed, together with a small quantity of absolute ethanol. In the latter tube, the contents of the first tube were poured into the second, and absolute ethanol was added to dissolve the crystals completely. The mixture was then stirred with a glass rod and allowed to stand. After standing for a week, colorless crystals separated as tablets insoluble in water — the inorganic part. After concentration of the aqueous solution, white crystals in the form of granules insoluble in water, with m.p. 160-162°, were precipitated. Yield 0.4 g.

Attempt to prepare the diethyl acetal of the ethyl ester of propionyl phosphinic acid [6]. To 5 g of the ethyl ester of propionylphosphinic acid, 4.6 g of ethyl orthoformate and 5 g of absolute ethanol were added. The mixture was allowed to stand ovemight at room temperature and then fractionated. The required fraction, boiling at a temperature of 140-142° at 14 mm, could not be separated. A fraction was separated with b.p. 118-119.5° 16 mm, in yield of 1 g; d_{20}^{20} 1.0715; n_D^{20} 1.4170.

Interaction of two molecules of ethyl orthopropionate with one molecule of phosphorus trichloride.

40 g of ethylorthopropionate was added to 15.7 g of phosphorus trichloride. Heat was evolved, and the solution came to a boil. When this process had ended, the mixture was heated for 2.5 hours on a water bath. A small white crystalline precipitate was obtained, and the solution assumed an almost green tinge. The reaction mixture was fractionated in a Widmer column.

There was obtained:

Fraction I, b.p. 99-100°; d_{20}^{20} 0.8889; n_D^{20} 1.3870; yield 21.5 g. Corresponds to ethyl propionate.

Fraction II, with b.p. 52-54° at 25 mm; d_{20}^{20} 1.0871; n_D^{20} 1.4344; yield 5.5 g. Corresponds to the chloranhydride of diethylphosphorous acid [7].

Analysis of phosphorus in Fraction II.

Found %: P 19.64, 19.75.
$C_4H_{10}O_2PCl$. Calculated %: P 19.87.

Interaction of one molecule of ethyl orthopropionate and one molecule of phosphorus trichloride

To 39.19 g of phosphorus trichloride, 50 g of ethyl orthopropionate was added. Evolution of heat accompanied by boiling was observed. When all the liquid had been added, a white precipitate formed. After boiling for two hours, the precipitate settled on the walls of the flask and assumed a yellow color. The reaction mixture was fractionated in a Widmer column. After three distillations, the following fractions were obtained.

Fraction I, b.p. 65-75°; 5.6 g.

Fraction II, b.p. 99-100.5°; 34 g; d_{20}^{20} 0.9772; n_D^{20} 1.3965. Corresponds to contaminated ethyl propionate.

Fraction III, b.p. 116-118°; 12 g; d_{20}^{20} 1.2373; n_D^{20} 1.4750. Corresponds to Menshutkin's chloranhydride [8].

Analysis of phosphorus in Fraction III.

Found %: P 21.09, 21.01

$C_2H_5OPCl_2$. Calculated %: P 21.08.

Interaction of three molecules of tetraethyl orthosilicate with four molecules of phosphorus trichloride

To 44.1 g of phosphorus trichloride, 50 g of tetraethyl orthosilicate was added. A trap was attached to collect the ethyl chloride. No visible signs of reaction were observed without heating. The reaction mixture was heated on the water bath for four hours at the temperature of boiling water. No ethyl chloride separated. The reaction mixture was fractionated in a Widmer column under reduced pressure and also at atmospheric pressure, and after three distillations the following fractions were obtained:

Fraction I, b.p. 116-118°; 27.5 g; d_0^{20} 1.3160. Corresponds to Menshutkin's chloranhydride [8].

Fraction II, b.p. 137-138°; 14.0 g; d_0^{20} 1.1290. Corresponds to diethoxy dichlorosilane [9], admixed with phosphorus-containing compounds.

Fraction III, b.p. 154-156;5°; 13.1 g; d_0^{20} 1.0460. Corresponds to triethoxy monochlorosilane [9].

Fraction IV, b.p. 63-86° at 26 mm; 7.2 g; d_0^{20} 1.0410.

Fraction V, a mixture with b.p. 120-150°; 8.8 g.

Analysis of phosphorus in Fraction 1*

Found %: P 21.10

$C_2H_5OPCl_2$. Calculated %: P 21.08

Analysis of Fraction II.

Found %: P 6.6; SiO_2 31.92.

$C_4H_{10}O_2SiCl_2$. Calculated %: P none; SiO_2 31.74.

Analysis of Fraction III

Found %: P none; SiO_2 31.10, 31.11.

$C_6H_{15}O_3SiCl$. Calculated %: P none; SiO_2 30.3.

Analysis of Fraction IV.

Found %: P 8.5; SiO_2 23.03.

$C_4H_{10}O_2PCl$. Calculated %: P 19.87; SiO_2 none.

SUMMARY

1. When three molecules of the ethyl ester of orthopropionic acid were reacted with one of phosphorus trichloride, the ethyl ester of propionic acid, triethyl phosphite, and the diethyl acetal of the ethyl ester of proponyl phosphinic acid were separated.

2. When two molecules of the ethyl ester of orthopropionic acid reacted with one molecule of phosphorus

* All analyses for phosphorus in the presence of silica were carried out by the method of amperometric titration [10].

trichloride, the ethyl ester of propionic acid and the chloranhydride of diethylphosphorous acid were obtained.

3. When one molecule of the ethyl ester of orthopropionic acid reacted with one molecule of phosphorus trichloride, the ethyl ester of propionic acid and Menshutkin's chloranhydride were obtained.

4. When three molecules of the tetraethyl ester of orthosilicic acid reacted with four molecules of phosphorus trichloride, Menshutkin's chloroanhydride and triethoxy monochlorosilane were obtained.

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BASIC NOMENCLATURE AND CLASSIFICATION OF LOW-MOLECULAR WEIGHT ORGANO-SILICON COMPOUNDS

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Principles for the classification of organo-silicon compounds have been repeatedly put forward in the literature. In 1905 [1], a terminology was proposed based on silane (SiH_4) termed "silicone", and (H_3SiOH), termed "silicanol". The names of all other compounds were derived from these. It was also proposed [2] that compounds containing the Si—Si bond should be called "silicases", and those containing Si—O—Si, "silicates". Later, Stock [3] proposed a nomenclature based on silicon hydrides; and compounds containing silicon and carbon atoms were named like the corresponding carbon compounds but with the prefix "silico"; thus, $CH_3CH_2SiH_3$ was silicopropane, and so on. Recently, the proposals of an American commission on organo-silicon nomenclature have been published [4]; the proposed nomenclature differs from Stock's mainly in the substitution of the prefix "sil" for "silico". The naming of organic groups is based on the Geneva System. New group terms have been introduced, e.g., "trisilonyl" for $H_3Si-SiH_2-SiH_2-$. In 1950, Kreshkov [5] proposed a nomenclature containing a number of important refinements. Thus, instead of the American commission's term "silazine" for nitrogen-containing compounds of the type $R_3SiNH[SiR_2NH]SiR_3$, he recommends "silamine".

In the nomenclatures discussed above, much attention is devoted to inorganic silicon compounds; this is especially so in the proposals of Stock and those of the American commission. For this reason, a large number of terms for inorganic atom groups are introduced, for example, $H_2Si<$ sililidine, $H_3SiNHSiH_2NH$ disilazanilamino, $H_3SiNHSiH_2O$ disilazanoxy, H_3SiSiH_2NH disilanilamino, etc. Many of these groups do not occur in organosilicon molecules, and they needlessly complicate nomenclature and terminology and make it difficult for the reader to study the organosilicon compounds.

At present the number of organosilicon compounds is considerable and it is growing every year. A separate classification and nomenclature are needed for organosilicon compounds, unencumbered by the nomenclature of compounds which should be considered in the inorganic chemistry of the silicons. We put forward the following basic classification and nomenclature for the organosilicon compounds, i.e., for silicon compounds which have carbon in addition to other elements as an essential constituent of the molecule.

The classification of low molecular weight organosilicon compounds which we put forward below is based on a rational nomenclature. The names of the simplest (first) compounds in a given class are used as the basis of the names of the compounds in that class. The silicon hydrides are used with advantage as starting materials in the classification, and all the remaining compounds are treated as derivatives of these, i.e., as substances derived from them by replacing one, two, three, or four hydrogen atoms by organic radicals or organic atom groups, and for certain classes of compounds with the simultaneous replacement of hydrogen by various atom or functional groups. The silicon hydrides constitute a class of compounds in which the silicon atoms are joined either to hydrogen or to other silicon atoms.

The general formula of the saturated silicon hydrides is Si_nH_{2n+2}. The simplest representative of this class of compound of silicon with hydrogen, SiH_4, is termed silane, its homolog $H_3Si-SiH_3$— disilane, $H_3Si-H_2Si-SiH_3$— trisilane, $H_3Si-SiH_2-SiH_2-SiH_3$ tetrasilane, and so on. Thus, the silicon hydrides form a homologous series, in which each successive member differs from the preceding one by the group SiH_2 (homologous difference).

When one or several hydrogen atoms in the homologous silicon hydride series is replaced by radicals or organic atoms groups such as

Radicals

Methyl CH_3-	Phenyl C_6H_5-	Naphthyl $C_{10}H_7-$	Chloromethyl $ClCH_2-$
Ethyl C_2H_5-	Tolyl $CH_3C_6H_4-$	Ethinyl $CH\equiv C-$	etc.,
Propyl C_3H_7-	Benzyl $C_6H_5-CH_2-CH_2-$	Chlorophenyl C_6H_4Cl-	
Butyl C_4H_9-	Vinyl $CH_2=CH-$	Chloroethyl $ClCH_2CH_2-$	

Atomic groups

Acetyl CH_3CO-	Acetamido $-CH_2CO-NH-$
Propionyl CH_3CH_2CO-	Toluyl $CH_3C_6H_4-CO-$
Benzoyl C_6H_5CO- etc.	Anilino C_6H_4NH-
Methoxy CH_3O-	etc.
Ethoxy C_2H_5O-	
Phenoxy C_6H_5O- etc.	

and hydrogen atoms joined to silicon are simultaneously replaced by functional groups: X (any halogen) $-OH$, $-NH_2$, O, etc. (oxygen is termed "oxy" to distinguish it from the OH-group, which is called "hydroxy") a corresponding homologous series is formed, consisting of halogen-containing organosilicon compounds, amines, etc. The position of the substituent groups in the aromatic nucleus is described in the usual way.

The following division of organosilicon compounds into large classes or series is most suitable for their study at the present time.

1. Substituted silanes

This class of compounds is formed by replacing one or several hydrogen atoms in the simple silicon hydrides SiH_4 or $H_3Si \cdot SiH_3$, etc., by the same or different radicals of the general fromula

$$C_nH_{2n+1}, \quad C_nH_{2n}, \quad C_nH_{2n-1}, \quad C_nH_{2n-7}, \text{ etc.}$$

If one radical is attached to the silicon atom, the compound is termed a monosubstituted silane, with two – a disubstituted, with three – a trisubstituted, and with four – a tetrasubstituted silane.

Substituted silanes having different radicals on the silicon atom are called mixed substituted silanes. The radical is named according to the accepted rules of organic nomenclature. Therefore, the names of the substituted silanes are derived from the name of the radical or radicals with the ending silane; hydrogen is not pronounced, for example:

$CH_3-CH_2-CH_2-CH_2-SiH_3$ – butylsilane

$CH_3-C(CH_3)_2-SiH_3$ – 1,1,1-trimethylmethylsilane

$CH_3-CH(CH_3)-CH_2-SiH_3$ – 1,1-dimethylethylsilane

$CH_3-CH_2-SiH_2-CH_3$ – methylethylsilane

$ClCH_2-SiH_3$ – 1-chloromethylsilane

$ClCH_2CH_2-SiH_3$ – 2-chloroethylsilane

$(CH_3)_3Si \cdot Si(CH_3)_3$ – hexamethyldisilane

$(CH_3)_3Si \cdot Si(CH_2CH_3)_3$ – 1-trimethyl-2-triethyldisilane

2. Esters of orthosilicic acid

Orthosilicic acid esters are formed when hydrogen in SiH_4 is replaced by organic atom groups, i.e., by alkoxy or aryloxy groups of the general formula $C_nH_{2n+1}O-$, $C_nH_{2n}O-$, etc. The name of the ester is composed from the name of the organic atom group, the ending silane and the prefixes di-, tri-, tetra- indicating the number of organic atom groups joined to silicon, for example $(CH_3O)_4Si$ – tetramethoxysilane; $(CH_3O)_2-Si-(OC_2H_5)_2$ – dimethoxydiethoxysilane; $C_6H_5O-Si-(OCH_3)_3$ – phenoxytrimethoxysilane, etc.

3. Halogen esters of orthosilicic acid

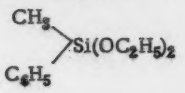
Halogen esters of orthosilicic acid are formed by replacing one, two, or three hydrogen atoms in silicon hydride SiH_4 by organic atom groups, i.e., by alkoxy groups of the general formula $C_nH_{2n+1}O-$ or aryloxy groups of the general formula $C_nH_{2n-7}-O-$ etc., while at the same time one, two, or three hydrogen atoms in SiH_4 are replaced by the same or different halogens (F, Cl, Br, and I). The halogen ester name is composed from the names of the organic groups, the halogen, and the ending silane. The number of atoms or groups joined to silicon is also

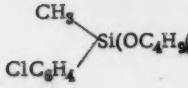
indicated, for example $(C_2H_5O)_3-SiCl$ – triethoxychlorosilane, $(C_2H_5O)(CH_3O)SiCl_2$ – ethoxymethoxydichlorosilane, etc.

4. Substituted esters of orthosilicic acid

Substituted esters of orthosilicic acid are formed by replacing one or more hydrogen atoms in the simplest silicon hydride, SiH_4, by the same or different organic radicals C_nH_{2n-1}, C_nH_{2n-7}, etc., while other hydrogen atoms joined to silicon are at the same time replaced by the same or different alkoxy or aryloxy groups of the general formula $C_nH_{2n+1}-O-$, $C_nH_{2n-5}-O-$, etc. If one radical is joined to the silicon atom the compound is termed a monosubstituted ester of orthosilicic acid; with two radicals, the corresponding disubstituted, and with three radicals, a trisubstituted orthosilicic ester. The names of the substituted orthosilicic esters are composed from the name of the organic radical, the names of the alkoxy or aryloxy groups (organic atom groups), and the ending silane. The number of organic radicals and the number of organic atom groups joined to silicon are indicated, for example:

$CH_3Si(OC_2H_5)_3$ – methyltriethoxysilane


– methylphenyldiethoxysilane

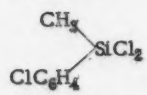

– methyl-3-chlorophenyldi-n-butoxysilane

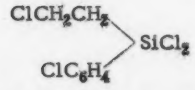
$ClCH_2CH_2-Si(OCH_2CH_2Cl)_3$ – 2-chloroethyltri-2-chloroethoxysilane, etc.

5. Alkyl and arylhalogenosilanes

Alkyl- and arylhalogenosilanes are formed by replacing one, two, or three hydrogen atoms in siliconhydride SiH_4 or $H_3Si\text{-}SiH_3$ by organic radicals while the remaining one, two, or three hydrogen atoms in the same silicon hydride are replaced by halogen (chlorine, fluorine, bromine, or iodine). If one radical is joined to the silicon atom, the compounds are called monoalkyl-(aryl)halogenosilanes; with two radicals, dialkyl-(aryl)halogenosilanes; and with three radicals, trialkyl-(aryl)halogenosilanes. The names of the alkyl- and arylhalogenosilanes are composed from the name of the organic radical, the name of the halogen, and the ending silane. The number of radicals is also indicated as well as the number of halogen atoms and the names of the other atoms and groups.

$C_6H_5SiCl_3$ – phenyltrichlorosilane

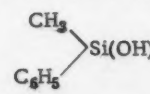

– methylchlorophenyldichlorosilane

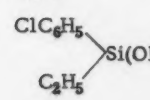

– 2-chloroethylchlorophenyldichlorosilane, etc.

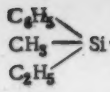
6. Organosilane hydroxyderivatives

Hydroxy derivatives of the organosilanes are formed by replacing one, two, or three hydrogen atoms in silicon hydride by organic radicals, while the remaining one, two, or three hydrogen atoms are replaced by hydroxyl groups. The terms mono-, di-, trihydroxylsilane derivative are used, according to the number of radicals joined to silicon. The name of the hydroxylsilane derivative is composed of the name of the organic radical, silane, and hydroxyl. The hydroxyl group is termed "hydroxy". The number of radicals and the number of hydroxyl groups, as well as the names of the atoms or atom groups in the radical are also indicated, for example:

$(C_2H_5)_2Si(OH)_2$ – diethyldihydroxysilane


– methylphenyldihydroxysilane

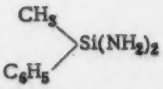

– chlorophenylethyldihydroxysilane



– phenylmethylethylhydroxysilane, etc.

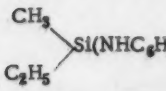
7. Alkyl- and arylaminosilanes

Alkyl- and arylaminosilanes are formed by replacing one, two, or three atoms of hydrogen in silicon hydride by organic radicals while the remaining one, two, or three hydrogen atoms in the same hydride are replaced by amino groups or by inorganic atom groups containing amino groups. Mono-, di-, and trialkyl (aryl)-aminosilanes are differentiated, according to the number of radicals joined to silicon in the molecule. The names of the alkyl(aryl)aminosilanes are composed from the names of the organic radical and the amino group, and the ending silane. For example:



– methylphenyldiaminosilane

$(CH_3)_3SiNHCH_3$ – trimethylmethylaminosilane



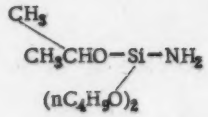
– methylethyldiphenylaminosilane

$(CH_3)_3SiNHSi(CH_3)_3$ – hexamethylaminodisilane

$(CH_3)_3SiCH_2NH_2$ – trimethylaminomethylsilane

8. Alkoxy(aryloxy)aminosilanes

Alkoxy-(aryloxy)aminosilanes are formed by replacing one, two, or three hydrogens in silicon hydride SiH_4 by organic atom groups, i.e., by alkoxy-(aryloxy) groups of the general formula $C_nH_{2n+1}-O-$, $C_nH_{2n-7}O-$, etc., while the remaining hydrogen atoms are replaced by amino groups. The names of the alkoxy-(aryloxy)amino-silanes are composed from the name of the organic atom group and the amino group, and the ending silane, together with the prefixes di- and tri-, indicating the number of organic atom groups and amino groups joined to silicon, for example:

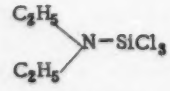


– isopropyloxydi-n-butyloxyaminosilane

$(C_4H_9O)_3SiNH_2$ – tri-tertiary butoxyaminosilane, etc.

9. Alkyl- and arylhalogenoaminosilanes

Alkyl- and arylhalogenoaminosilanes are formed by replacing one, two, or three hydrogen atoms in the simplest silicon hydride by organic atom groups containing nitrogen, while the remaining one, two, or three hydrogen atoms are replaced by halogen (chlorine, fluorine, bromine, or iodine). The names of alkyl-arylhalo-genoaminosilanes are composed from the name of the organic atom group, the name of the halogen, and the ending silane, for example:

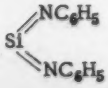


– diethylaminotrichlorosilane

$(C_6H_5NH)_2SiCl_2$ – diphenylaminodichlorosilane, etc.

10. Alkyl-aryliminosilanes

Alkyl-(aryl)iminosilanes are formed by replacing all the hydrogens in silicon hydride SiH_4 by imino groups =NR, or two hydrogens by an imino group and the remaining two by organic radicals or atom groups or by other atoms. The names of these compounds are composed of the radical name, the names of the organic groups, and the name of the imino group with the ending silane, for example:



– diphenyliminosilane

$(C_6H_5NH)_2Si{=}NC_6H_5$ – diphenylaminophenyliminosilane

$(C_6H_5)_2Si{=}N(C_6H_5)$ – diphenylphenyliminosilane

11. Silicon isocyanates

The silicon isocyanates are formed by replacing one, two, three, or four hydrogen atoms in silicon hydride SiH_4 by the group $-N{=}C{=}O$, while the remaining one, two, or three hydrogen atoms in the same silicon hydride are replaced by radicals, organic atom groups, or any other atom. The names of the silicon isocyanates are composed from the radical or organic atom group name, the name of the isocyanate group, and the ending silane. The number of radicals, organic atom groups, and the number of isocyanate groups are also indicated, for example:

$(CH_3)_2Si(NCO)_2$ – dimethyldiisocyanatesilane, etc.

The names of the silicon isothiocyanates are constructed in the same way, but the prefix "thio" is used, for example:

$(C_2H_5)Si(NCS)_3$ – ethyltrithioisocyanatesilane

12. Organometallic compounds of silicon

The organometallic compounds of silicon are formed by replacing one or more hydrogen atoms in SiH_4 by a metal (Na, K, Li, etc.), while the remaining three hydrogen atoms in the same silicon hydride are replaced by radicals, organic atom groups, or by any other atom. The names are composed from the radical name, the name of the atom group or the other atom, the name of the metal and the ending silane. The number of groups, radicals, etc. is also indicated, for example:

$(CH_3)_3SiLi$ – trimethyllithiumsilane

$(CH_3)_3SiOLi$ – trimethyllithiumoxysilane, etc.

13. Thioethers

Thioethers are formed by replacing one, two, three, or four hydrogen atoms in SiH_4 by the groups $C_nH_{2n+1}S-$, $C_nH_{2n-1}S-$, while the remaining one, two, or three hydrogen atoms in the same silicon hydride are replaced by radicals, by organic atom groups, or by other atoms or groups. The names of the thioethers are composed from the name of the thio group, the number of thio groups present, and the names of the radicals, organic atom groups, or other atoms. In addition, the number of these is indicated, for example:

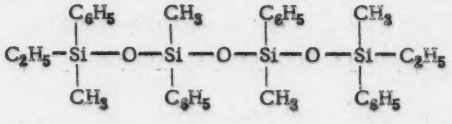
$(C_2H_5S)_3SiC_6H_5$ – trithioethylphenylsilane

$(BrC_6H_4S)_4Si$ – tetra-4-bromophenylthiosilane

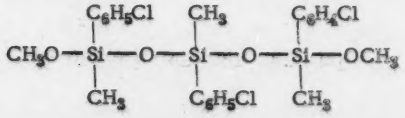
$[(CH_3)_3(CS)_3Si]_2O$ – hexatertiary butylthiodisiloxane

14. Organosiloxanes

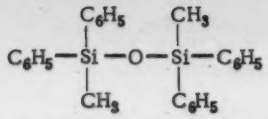
When organosilicon hydroxy derivatives undergo condensation, compounds are formed whose molecules contain siloxane Si–O–Si groups of atoms. These compounds, which are characterized by a cyclic or a chain molecular structure, are formed by the linking of alternate atoms of silicon and oxygen; we call them organosiloxanes. The classification and nomenclature of the high molecular weight compounds, the "organopolysiloxanes", and others will be given in a later paper. The names of the organosiloxanes are composed from the names of the radical or organic atom groups and their number, the number of siloxane groups in the molecule, and the ending – siloxane. The positions of the organic radicals and atom groups are also indicated, for example:



1,4-diethyl-1,2,3,4-tetraphenyl-1,2,3,4-tetramethyltetrasiloxane

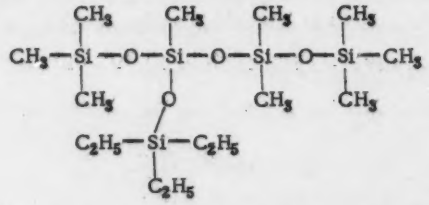


1,3-methoxy-1,2,3-chloro-3-phenyl-1,2,3-trimethyltrisiloxane



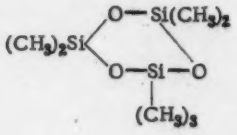
1,2-phenyl-1,2-methyl-1,2-phenyldisiloxane , etc.

When the organosilicon compound has a branched chain, the naming follows the principles usually employed for organic compounds, for example:

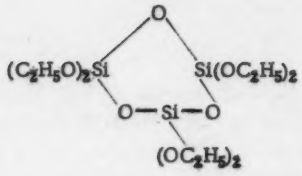


1,2,3,4-nonamethyl-2-triethylsiloxytetradisiloxane

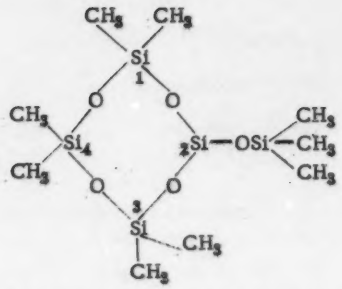
The prefix cyclo is used for cyclic organosiloxanes, for example:



– hexamethylcyclotrisiloxane

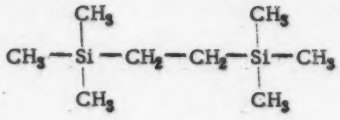


– hexamethylcyclotrisiloxane, etc.

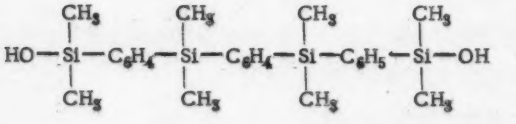


– 1,2,3,4-heptamethyl-2-trimethylsiloxycyclotetrasiloxane

Compounds with mixed chains, the molecules of which have silicon atoms joined to one another by divalent radicals or organic atom groups, have names derived from the radical or group names, for example:



– ethylenehexamethyldisilane



– triphenylene-1,4-hydroxy-1,1,2,2,3,3,4,4,-octamethyltetrasilane.

SUMMARY

1. A classification and nomenclature for the low-molecular-weight organosilicon compounds are proposed.
2. The names of the simplest (first) compounds in a given class are proposed as a basis for naming low-

molecular weight organosilicon compounds. The silicon hydrides are used as fundamental substances in the classification, and all other compounds are regarded as derivatives of these.

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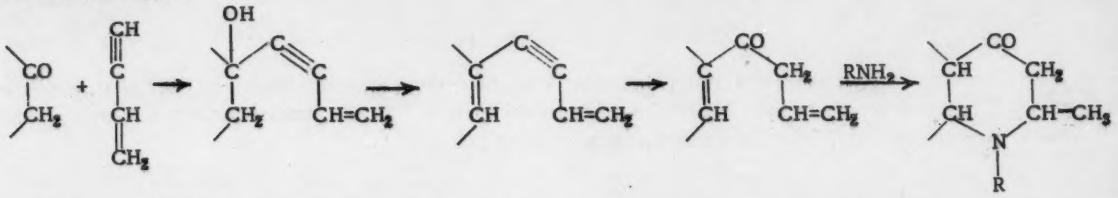
ACETYLENE DERIVATIVES

COMMUNICATION 150. HETEROCYCLIC COMPOUNDS

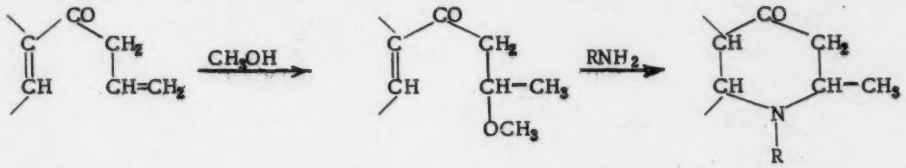
XXVI. THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS CONTAINING A CONDENSED 4-PIPERIDONE NUCLEUS

L. N. Nazarov, L. I. Ukhova, and V. A. Rudenko

The synthesis of 4-piperidones is of considerable interest, because they are important intermediates for the preparation of many pharmaceutical products of high analgesic, spasmolytic, and anesthetic activity. A few years ago a new simple method for the synthesis of 4-piperidones, starting from vinylallylketones [1] and ammonia or primary amines, was developed in our laboratory. The complete route to the 4-piperidones by this method may be illustrated as follows.

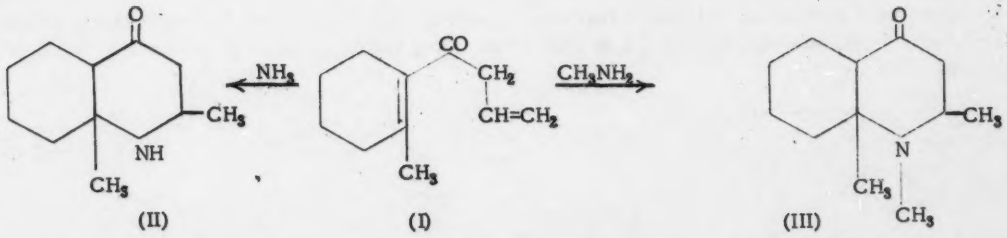


The 4-piperidones are also easily obtained by the action of ammonia or primary amines on the corresponding methoxyketones which are formed by the addition of methanol to vinylallylketone.



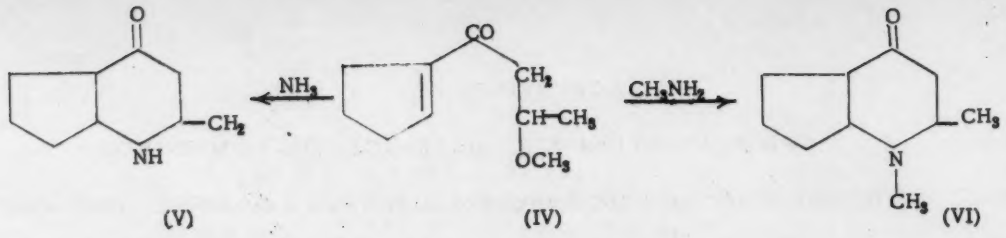
By means of this reaction, numerous 4-piperidones with various aliphatic and aromatic substituents in the piperidine nucleus were prepared. It was of interest to find if this method was applicable to the preparation of more complex polycyclic compounds containing the condensed 4-piperidone nucleus and angular methyl groups. We have therefore studied the reaction of ammonia and methylamine with various allyl-Δ^1-cyclenylketones and their corresponding methoxyketones.

2,9-Dimethyl-4-ketodecahydroquinoline (II) and 1,2,9-trimethyl-4-ketodecahydroxyquinoline (III) were obtained in about 80% yield by the interaction of allyl-2-methyl-Δ^1-cyclohexenylketone (I) [2] with ammonia and methylamine.



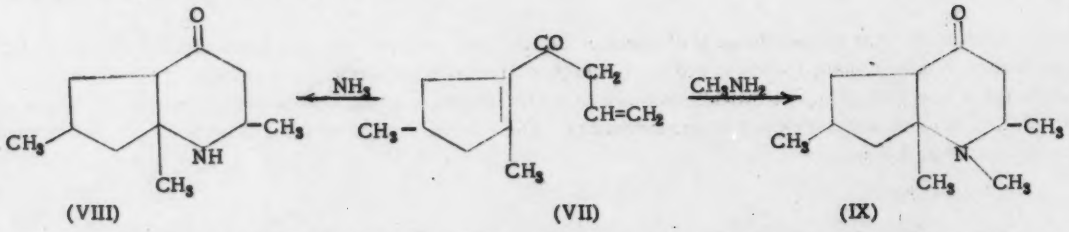
By the interaction of β-methoxypropyl-Δ^1-cyclopentenylketone (IV) [3] with ammonia and methylamine, 2-methyl-4-ketoperhydro-1-pyrindine (V) and 1,2-dimethyl-4-ketoperhydro-1-pyrindine (VI) are obtained in about 80% yield. (See top of following page.)

By the interaction of allyl-2,4-dimethyl-Δ^1-cyclopentenylketone (VII) and its corresponding methoxyketone [4] with ammonia and with methylamine, 2,6,7a-trimethyl-4-ketoperhydro-1-pyrindine (VIII) and 1,2,6,7a-tetra-



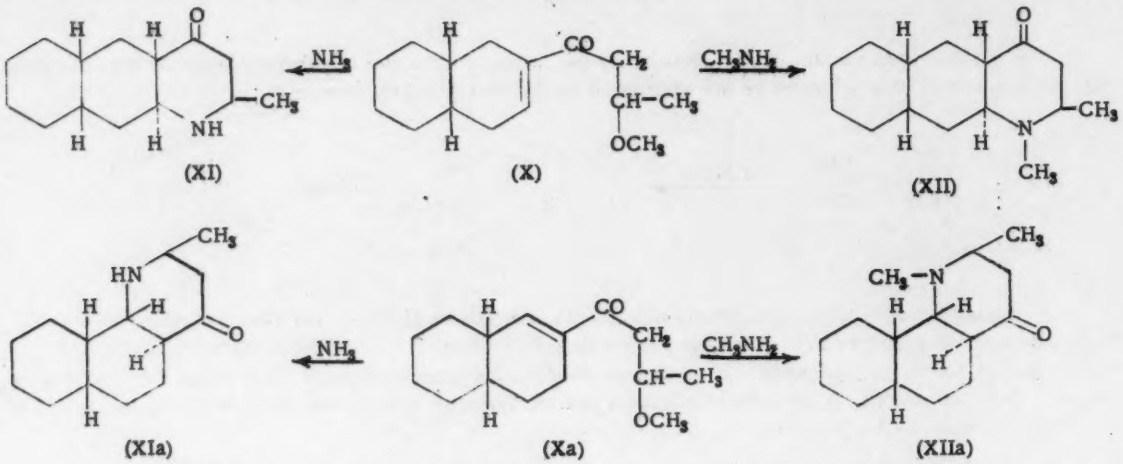
(V) (IV) (VI)

methyl-4-ketoperhydropyrindine (IX) are obtained:



(VIII) (VII) (IX)

The action of ammonia and methylamine on β-methoxypropyl-2-octalylketone (X) and (Xa), which was obtained from cis-β-decalone, gave 2-methyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XI) or (XIa) and 1,2-dimethyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XII) or (XIIa):

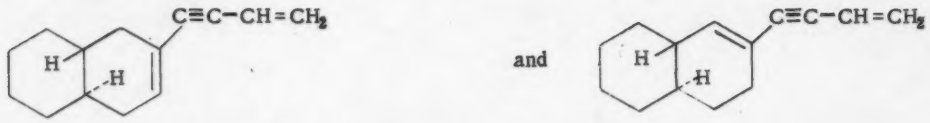


(XI) (X) (XII)

(XIa) (Xa) (XIIa)

Hückel and Friedrich [5] have shown that dehydration of cis-β-decalones gives a mixture of Δ^1- and Δ^2-octalins, the relative quantities varying with the dehydrating agent.

Nazarov and Burmistrova [6] showed that vinylethynyl alcohol, obtained by the condensation of trans-β-decalone with vinylacetylene, also gives a mixture of the two 2-vinylethynyloctalines in almost equal proportions on dehydration:



From these results it might be expected that in our dehydration of vinylethynyl alcohol, obtained by the condensation of cis-β-decalone with vinylacetylene, a mixture of the two cis-2-vinylethynyloctalins, Δ^1- and Δ^2-, would be obtained; on dehydration these would give a mixture of the corresponding two cis-allyl-2-octalylketones. We therefore attempted to separate these ketones, in order to cyclize the individual compounds with ammonia and methylamine. However, we did not succeed in separating either the cis- or the trans-allyl-2-octalylketone, since they did not crystallize even when cooled to −75°.

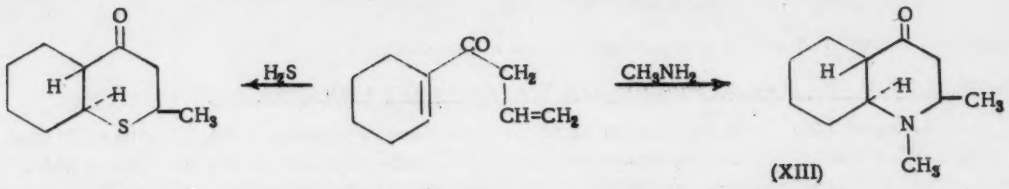
Since the cyclization product of the methoxyketones (X) or (Xa) with methylamine gave only one picrolonate with m.p. 201-203°, it may be supposed that in this cyclization one tricyclic ketone (XII) or (XIIa) is mainly formed, and the second is either not formed at all or is present in negligible quantity so that its separation is difficult.

The cyclization product of the methoxyketone (X) or (Xa) with ammonia did not give crystalline derivatives with either picric or picrolonic acid even on long standing. Since the position of the double bond in the methoxyketone (X) or (Xa) has not been proved, we ascribe formula (XII) or (XIIa) to the 1,2-dimethyl-4-ketoperhydrobenzoquinoline obtained, and formula (XI) or (XIa) to the 2-methyl-4-ketoperhydrobenzoquinoline.

The N-methylated compounds (III), (VI), (IX), and (XII) or (XIIa) were freed from impurities in the form of the corresponding imines [7] before analysis, by heating on the water bath with dilute hydrochloric acid, and after the usual treatment they were separated in the pure state.

In order to establish the steric structure of the 4-ketodecahydroquinolines (II), (III), and (XIII) obtained, these were heated with methanolic sodium methoxide. In all cases the starting material was recovered from the reaction mixture; this was proved by the fact that mixed samples of the picrates showed no depression in the melting points. By analogy with the α-decalones [8], the inability of the 4-ketodecahydroquinolines (II), (III), and (XIII) to isomerize under the influence of sodium methoxide may be taken as proof of the trans-configuration of these ketones.

Consequently, when allyl-Δ^1-cyclohexenylketones are cyclized with ammonia and primary amines, a piperidine nucleus joined at the trans position to another ring is formed; this was shown previously in our laboratory for the cyclization of the allyl-Δ^1-cyclohexenylketone with hydrogen sulfide [9]:



(XIII)

There is no doubt that the 4-ketoperhydrobenzoquinolines (XI) and (XII) also have the trans structure at the position where the 4-piperidone nucleus is fused with decalin.

It is also probable that the 4-ketoperhydro-1-pyrindines (V), (VI), and (IX) also have the trans structure; they did not change on heating with sodium methoxide, as was shown by the mixed melting point of the picrates.

Finally, it should be mentioned that the synthesis of 4-piperidones from the most diverse vinylallylketones, ammonia, and primary amines is the most general and the simplest method at present available for preparing these interesting and important compounds. It enables 4-piperidones with different nuclear substituents to be obtained, and also polycyclic compounds containing a condensed 4-piperidone nucleus and angular alkyl groups.

EXPERIMENTAL

1,2,9-Trimethyl-4-ketodecahydroquinoline (III)

A solution of 300 g of allyl-2-methyl-Δ^1-cyclohexenylketone (I) (m.p. 126-128° at 11 mm; n_D^{18} 1.4885 [2]) and 420 g of 33% aqueous methylamine in 270 ml of methanol was heated in a sealed metal tube at 60-70° for 7 hours. The tube was opened, the methanol and excess methylamine distilled off on the water bath under slightly reduced pressure, the residue acidified with hydrochloric acid (1:1), and the neutral products extracted with ether. The reaction product was separated by means of solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had first been distilled off. There was obtained 254 g of 1,2,9-trimethyl-4-ketodecahydroquinoline (III) with b.p. 110-115° at 4 mm; n_D^{19} 1.5020. In order to remove possible imino-derivative impurities [7], 20 g of the compound was mixed with 30 ml of dilute hydrochloric acid (1:3) and heated for 1 hour on the boiling water bath. After cooling with ice water, the solution was saturated with solid alkali, and the base was extracted with ether, dried over sodium sulfate, and distilled under reduced pressure, after the ether had been distilled off. The product consisted of 15.1 g of pure 1,2,9-trimethyl-4-ketodecahydroquinoline in the form of a colorless, mobile liquid with a typical amine odor and b.p. 103-104° at 3 mm; n_D^{20} 1.5018; d_4^{20} 1.004; found MR 57.33; calculated MR 57.17.

$C_{12}H_{21}ON$. Found %: N 7.19, 7.33. Calculated %: N 7.12

After recrystallization from aqueous ethanol, the picrate melted at 195-196°.

Attempt to isomerize 1,2,9-trimethyl-4-ketodecahydroquinoline

A solution of 0.15 g of metallic sodium in 65 ml of methanol was added to 5.4 g of 1,2,9-trimethyl-4-ketodecahydroquinoline (b.p. 103-104° at 3 mm; n_D^{20} 1.5018). The solution was refluxed for 5 hours, and then neutralized with acetic acid, after which the methanol was distilled off. The residue was dissolved in 8 ml of water, the solution was saturated with potash, the product extracted with ether, dried over sodium sulfate, and distilled under reduced pressure. Four grams of the starting 1,2,9-trimethyl-4-ketodecahydroquinoline with b.p. 106-107° at 3 mm; n_D^{20} 1.4995 was obtained. The picrate melted at 194-195° and gave no depression with the picrate of the starting material.

2,9-Dimethyl-4-ketodecahydroquinoline (II)

A solution of 30 g of allyl-2-methyl-Δ^1-cyclohexenylketone, (b.p. 126-128° at 11 mm; $n_D^{18.5}$ 1.4884 [2]), and 70 g of 30% aqueous ammonia in 120 ml of methanol was heated in a sealed metal tube for 6 hours at 70-75°. The methanol and excess ammonia were distilled off under reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), and the neutral product extracted with ether. The base was carefully separated, with ice-water cooling, by means of solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been first distilled off. The product, 26 g of 2,9-dimethyl-4-ketodecahydroquinoline (II), was a colorless mobile liquid with a weak ammoniacal odor and b.p. 99-100° at 3 mm; n_D^{20} 1.5021; d_4^{20} 1.015; found MR 52.49; calculated MR 52.21.

Found %: N 7.42, 7.29.
$C_{11}H_{19}ON$. Calculated %: N 7.72.

The picrate on recrystallization from ethanol melted at 200-201°.

Attempt to isomerize 2,9-dimethyl-4-ketodecahydroquinoline

A solution of 0.2 g of metallic sodium in 65 ml of methanol was added to 8 g of the base (II) (b.p. 99-100° at 3 mm; n_D^{20} 1.5021). The solution was boiled for 5 hours. After treatment as described above and distillation under reduced pressure, 7.3 g of the initial 2,9-dimethyl-4-ketodecahydroquinoline, with b.p. 100-101° at 3 mm; n_D^{20} 1.4997, was obtained. The picrate melted at 199-200°, and gave no depression with the picrate of the initial material.

1,2-Dimethyl-4-ketoperhydro-1-pyrindine (VI)

A solution of 50 g of β-methoxypropyl-Δ^1-cyclopentenylketone (IV) (b.p. 85-86° at 3 mm; n_D^{23} 1.4803 [3]) and 80 g of 25% aqueous methylamine in 60 ml of methanol was heated in a sealed metal tube for 5 hours at 70°. The methanol and excess methylamine were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), and the neutral product extracted with ether. The reaction product was separated by the addition of solid alkali with ice-water cooling, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been removed. 39 g of 1,2-dimethyl-4-ketoperhydro-1-piperindine (VI), with b.p. 88-89° at 2 mm; n_D^{24} 1.4922.

After heating the product (39 g) with 7% hydrochloric acid (125 ml) at 70-80° for 1 hour, 35.4 g of pure 1,2-dimethyl-4-ketoperhydro-1-pyrindine (VI) with b.p. 86-87° at 2 mm; n_D^{20} 1.4912; d_4^{20} 1.0104, was obtained. Found MR 47.94; calculated MR 47.93.

Found %: N 8.48, 8.56.
$C_{10}H_{17}ON$. Calculated %: N 8.37.

After recrystallization from ethanol the picrate melted at 164.5-165°.

An attempt to isomerize 1,2-dimethyl-4-ketoperhydro-1-pyrindine in methanolic sodium methoxide solution, as described above, afforded only the initial material, as shown by a melting point test of the mixed picrates.

2-Methyl-4-ketoperhydro-1-pyrindine (V)

A solution of 40 g of β-methoxypropyl-Δ^1-cyclopentenylketone (b.p. 85-86° at 3 mm; n_D^{20} 1.4803 [3]), and 100 g of 25% aqueous solution of ammonia in 75 ml of methanol was heated in a sealed metal tube for six hours at 60°. The methanol and excess ammonia were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), and the neutral products extracted with ether. The base was separated by the addition of solid alkali with ice-water cooling, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had first been distilled off. The yield was 27.2 g of 2-methyl-4-ketoperhydro-1-

pyrindine (V) with b.p. 85-86° at 1 mm; n_D^{20} 1.4982; d_4^{20} 1.0381; found MR 43.27; calculated MR 42.97.

Found %: N 9.13, 8.98.

$C_9H_{15}ON$. Calculated %: N 9.14.

The picrate after recrystallization from alcohol melted at 161-162°.

An attempt to isomerize 2-methyl-4-ketoperhydro-1-pyrindine by heating for 4 hours in methanolic sodium methoxide solution yielded only the initial material, as was proved by a mixed picrate melting point test.

1,2,6,7a-Tetramethyl-4-ketoperhydro-1-pyrindine (IX)

A solution of 25 g of a mixture of allyl-2,4-dimethyl-Δ^1-cyclopentenylketone (VII) with its corresponding methoxyketone (b.p. 90-98° at 4 mm; $n_D^{22.5}$ 1.4795 [4]) and 45 g of 25% aqueous methylamine in 50 ml of methanol was heated in a sealed metal tube at 70° for 4 hours. The methanol and excess methylamine were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), and the neutral product extracted with ether; the base was carefully separated with solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure, after the ether had first been distilled off. A yield of 17 g of 1,2,6,7a-tetramethyl-4-ketoperhydro-1-pyrindine (IX) with b.p. 94-97° at 4mm; n_D^{20} 1.4915, was obtained. Residue of resinous substance, 5.3 g.

When the 17 g of base (IX) thus obtained was heated with 45 g of 7% hydrochloric acid at 70-80° for one hour, 12.9 g of pure base (IX) with b.p. 90-92° at 4 mm was obtained; n_D^{20} 1.4894; d_4^{20} 0.9800; found MR 57.46; calculated MR 57.16.

Found %: N 7.01, 7.29.

$C_{12}H_{21}ON$. Calculated %: N 7.12.

The picrate, recrystallized from alcohol, melted at 184-185°.

An attempt to isomerize 1,2,6,7a-tetramethyl-4-ketoperhydro-1-pyrindine in methanolic sodium methoxide solution yielded only the initial material, as was shown by a mixed picrate melting point test.

2,6,7a-Trimethyl-4-ketoperhydro-1-pyrindine (VIII)

A solution of 22 g of a mixture of allyl-2,4-dimethyl-Δ^1-cyclopentenylketone (VII) and the corresponding methoxyketone (b.p. 90-98° at 4 mm; n_D^{22} 1.4705 [4]) and 45 g of 25% aqueous ammonia in 75 ml of methanol was heated in a sealed metallic tube at 70° for 4 hours. The methanol and excess ammonia were distilled off under slightly reduced pressure, the residue acidified with dilute hydrochloric acid (1:1), the neutral products extracted with ether. The base was carefully separated with solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure, after the ether had first been distilled off. A yield of 15.6 g of 2,6,7a-trimethyl-4-ketoperhydro-1-pyrindine (VIII) with b.p. 85-86° at 3.5 mm was obtained; n_D^{20} 1.4842; d_4^{20} 0.9849; found MR 52.64; calculated MR 52.21.

Found %: N 8.14, 7.94.

$C_{11}H_{19}ON$. Calculated %: N 7.72.

The picrate separated from an alcoholic solution after standing for several months, and after recrystallization from alcohol melted at 164.5-165.5°.

Cis-2-vinylethynyl-2-decalol

To 180 g of powdered potassium hydroxide and 1100 ml of dry ether in a round-bottomed flask a mixture of 315 g of cis-β-decalone (b.p. 113-114° at 14 mm; n_D^{20} 1.4910) and 200 g of vinylacetylene dissolved in 250 ml of dry ether was added with constant stirring and cooling to −10° over 3 hours. The reaction mixture was stirred and kept cool for 6 hours, and on the following day it was treated with water (250 ml). The product was extracted with ether, neutralized with 8% hydrochloric acid, dried over sodium sulfate, and distilled under reduced pressure after the ether had first been distilled off. A yield of 280 g of cis-2-vinylethynyl-2-decalol with b.p. 131-132° at 6 mm and n_D^{18} 1.5340 was obtained. Trans-2-vinylethynyl-2-decalol was obtained from trans-β-decalone and had b.p. 116-118° at 4 mm; n_D^{20} 1.5228 [6].

Cis-2-vinylethynyloctalin

A mixture of 280 g of cis-2-vinylethynyl-2-decalol and 280 g of 50% sulfuric acid was vigorously stirred at 60° for 8 hours. At the end of the reaction the hydrocarbon layer was separated, neutralized with sodium carbonate solution, dried over sodium sulfate, and distilled under reduced pressure. A yield of 160 g of cis-2-vinylethynyloctalin was obtained; it had b.p. 100-102° at 2 mm; n_D^{20} 1.5485. Trans-2-vinylethynyloctalin has

b.p. 100-102° at 3 mm; n_D^{20} 1.5482 [6].

β-Methoxypropyl-2-octalylketone (X) or (Xa)

A mixture of 165 g of cis-2-vinylethynyloctalin, 3.5 g of concentrated sulfuric acid, 50 g of mercuric sulfate (added in three portions), and 1230 g of 95% methanol was stirred at 60° for 7 hours. The methanol was distilled off under reduced pressure, the product extracted with ether, neutralized with sodium carbonate solution, dried over sodium sulfate, and distilled under reduced pressure, after the ether had first been distilled off. A yield of 160.7 g of β-methoxypropyl-2-octalylketone (X) or (Xa) was obtained; it had b.p. 150-154° at 7 mm; n_D^{20} 1.5120.

Allyl-2-octalylketone

30 g of the bicyclic methoxyketone (X) or (Xa) and 0.1 g of p-toluenesulfonic acid were heated for 20 minutes under vacuum (130°, 100 mm). On distillation, 20 g of allyl-2-octalylketone with b.p. 133-135° at 3 mm was obtained; $n_D^{20.5}$ 1.5220. Allyl-2-octalylketone obtained from trans-β-decalone has b.p. 133.5-135° at 4.5 mm; n_D^{20} 1.5234 [6]. The product failed to crystallize on long standing at −75°.

1,2-Dimethyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XII) or XIIa)

A solution of 50 g of β-methoxypropyl-2-octalylketone (X) or (Xa) (b.p. 150-155° at 7 mm; n_D^{20} 1.5120) and 60.8 g of 25% aqueous solution of methylamine in 150 ml of methanol was heated in a sealed metal tube for 6 hours at 70°. The methanol and excess methylamine were distilled off under slightly reduced pressure; the residue was acidified with dilute hydrochloric acid (1:1), and the neutral product was extracted with ether. The reaction product was separated with solid alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been removed. A yield of 25.3 g of 1,2-dimethyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XII) or (XIIa) with b.p. 145-152° at 3mm was obtained; n_D^{19} 1.5221, and a resinous residue, 5.1 g.

When the product (25 g) was heated to 80° for one hour with 7% hydrochloric acid (60 ml), 20.6 g of the p pure base with b.p. 142-143° at 3mm was obtained; n_D^{20} 1.5210; d_4^{20} 1.0317; found MR 69.44; calculated MR 68.82.

Found %: N 5.56, 5.61.

$C_{15}H_{25}ON$. Calculated %: N 5.95.

The picrate separated as an oil. The picrolonate, when recrystallized from aqueous alcohol, melted at 201-203° with decomposition. Distillation of the neutralized reaction products yielded 13 g of the initial methoxyketone with b.p. 136-138° at 4 mm; n_D^{20} 1.5110.

2-Methyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XI) or (XIa).

A solution of 20 g of β-methoxypropyl-2-octalylketone (X) or (Xa) (b.p. 150-154° at 7 mm; n_D^{20} 1.5120) and 44 g of 25% aqueous ammonia in methanol was heated in a sealed metal tube for 5 hours at 70°. The methanol and excess ammonia were distilled off, the residue treated with dilute hydrochloric acid (1:1), and the neutral substances extracted with ether. The base was separated with alkali, extracted with ether, dried over sodium sulfate, and distilled under reduced pressure after the ether had been removed. A yield of 9.6 g of 2-methyl-4-ketoperhydro-6,7-(or 7,8)-benzoquinoline (XI) or (XIa) was obtained; it was a thick, colorless liquid with a typical amine odor: b.p. 140-142° at 2 mm; n_D^{20} 1.5196; d_4^{20} 1.0435; found MR 64.38; calculated MR 63.86.

Found %: N 6.47, 6.38.

$C_{14}H_{23}ON$. Calculated %: N 6.32.

The picrate failed to separate from alcoholic solution even after 4 months standing. Distillation of the neutral products yielded 4.7 g of the initial methoxyketone with b.p. 135-138° at 3 mm; n_D^{20} 1.5110.

SUMMARY

1. A number of polycyclic compounds, containing the 4-piperidone nucleus condensed with cyclohexane, cyclopentane, and decalin, have been synthesized. Some of the compounds obtained contain angular methyl groups.

2. It has been shown that the method developed in our laboratory for the synthesis of 4-piperidones from vinylallylketones and ammonia and primary amines is applicable to the preparation of the most diverse polycyclic compounds with condensed 4-piperidone nuclei.

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* See Consultants Bureau Translation, p. 2079 ff.

** See Consultants Bureau Translation, p. 2091 ff.

*** See Consultants Bureau Translation, p. 683 ff.

**** See Consultants Bureau Translation, p. a-621 ff.

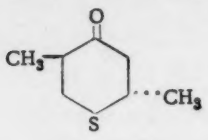
COMMUNICATION 152. HETEROCYCLIC COMPOUNDS.

XXVIII. THE SYNTHESIS OF SOME DERIVATIVES OF TETRAHYDRO-γ-THIOPYRONES

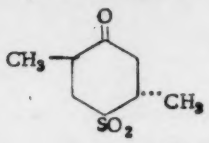
I. N. Nazarov and A. I. Kuznetsova

In a previous paper [1] we described a number of acids of the thiopyran series which were synthesized in order to determine their physiological activity. It also seemed of interest to prepare semicarbazones and thiosemicarbazones of the tetrahydro-γ-pyrones and their corresponding sulfones, since several thiosemicarbazones are known to have antitubercular activity [2,3].

By the interaction of trans-2,5-dimethyltetrahydro-1-thiopyran-4-one (I), which we have previously described [4] and its corresponding sulfone (II) with hydroxylamine sulfate in the presence of sodium acetate, the corresponding oximes (III) and (IV) were obtained in good yield.



(I)



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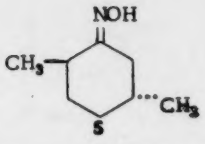

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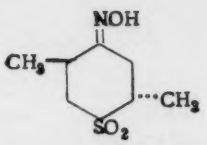
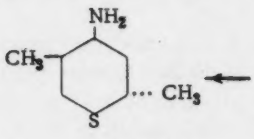


(IV)

Reduction of the oxime (III) afforded two geometric isomers of the corresponding amine (V) and (VI)



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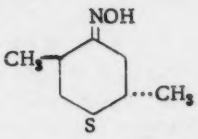

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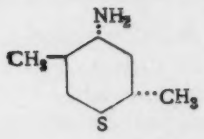
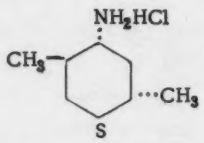


(VI)

It is known that oximes of the cyclohexane and piperidine series [5] yield trans amines when they are reduced in alkaline media, but in acid media cis structures are produced. Reduction of the oxime (III) by metallic sodium in absolute alcohol afforded 2,5-dimethyltetrahydro-1-thiopyran-4-amine (VI) in 55% yield; by analogy with the cyclohexane and piperidine compounds this must have the trans structure.

When dry hydrogen chloride was passed through an alcoholic solution of the amine (VI), the amine hydrochloride (VII) was formed; in the same way, carbon dioxide gave the corresponding carbonate. On treatment with acetic anhydride the amine (VI) gave the acetyl derivative (VIII); with benzoyl chloride in pyridine it gave the benzoyl derivative (IX)



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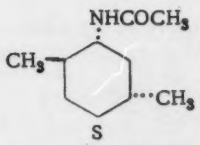

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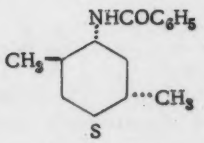
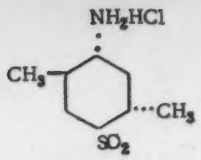
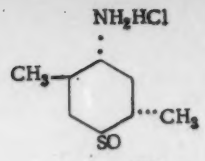


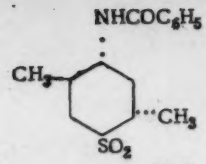
(IX)

On oxidation of the amine hydrochloride (VII) with 30% hydrogen peroxide solution in glacial acetic acid, the corresponding sulfone (X) was obtained; oxidation with 17% hydrogen peroxide in glacial acetic acid gave the the sulfoxide (XI). The sulfone (XII) was obtained by the interaction of the benzoyl derivative (IX) with 30% perhydrol solution in glacial acetic acid: (see top of following page).

Attempts to reduce the oxime (III) in neutral or acid medium in order to obtain the second possible stereoisomer of the amine (V) gave negative results. The catalytic hydrogenation of the oxime (III) could not be effected either in dioxan in the presence of Pd on calcium carbonate or in absolute alcohol saturated with hydrogen chloride in the presence of Pd on carbon. Reduction of the oxime (III) with the aid of zinc in alcohol


(X)

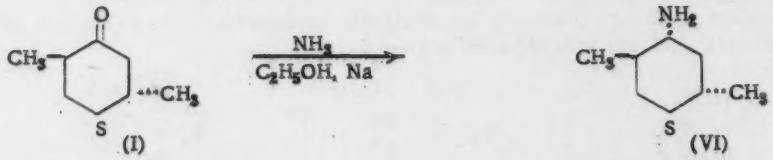

(XI)


(XII)

solution saturated with hydrogen chloride, or with sodium amalgam in acetic acid solution afforded only traces of the amine (VI).

As is known, primary amines of the cyclohexane series are obtained in good yield by the catalytic hydrogenation of cyclohexanones in the presence of ammonia. Colloidal platinum [6] or Raney nickel [7] may be used as a catalyst. For some of the aliphatic ketones this reaction may be effected by the action of metallic sodium in alcoholic ammonia solution [8].

We attempted to use the method described above to prepare amines of the thiopyrone series. The action of metallic sodium on the thiopyrone (I) in alcoholic ammonia solution gave the amine (VI) as the hydrochloride in 14% yield:

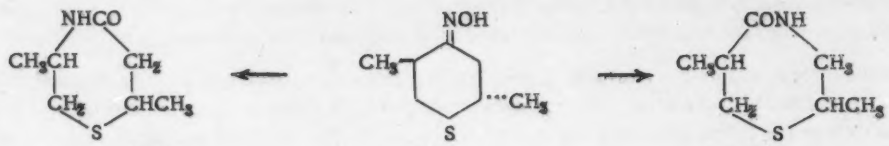

(I) (VI)

An attempt to hydrogenate the sulfone (II) in alcoholic solution of ammonia under normal pressure in the presence of Raney nickel gave only the unchanged starting material; the hydrogenation does not take place under these conditions.

Thus, by reduction of the oxime (III) and reduction of the thiopyrone (I) in ammonia solution, we only obtained one stereoisomer of the amine (VI).

The Beckmann rearrangement of ketoximes to substituted amides is well known and has been extensively studied in the aliphatic, aromatic, and heterocyclic series with the use of the most diverse reagents [9]. Rearrangement of the oximes of the cyclohexane series has been effected with sulfuric acid, phosphorus pentoxide, or benzenesulfonyl chloride [10], and has found practical use in the synthesis of artificial fibers.

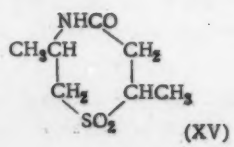
However, the rearrangement of oximes of the thiopyran series has not yet been studied. As with the cyclohexane oximes, here also the formation of lactams of two thioaminoacids may take place in the following manner:

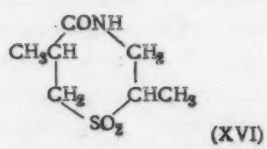

(XIII) (I) (XIV)

Heating of the oxime (I) with 70% sulfuric acid produced only one lactam (XIII) or (XIV). The use of 50% acid led to hydrolysis of the oxime, and more concentrated acids (80-90%) lowered the lactam yield.

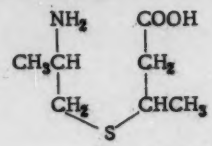
Rearrangement of the oxime (I) did not take place in the present of p-toluenesulfonyl chloride either in pyridine or in 20% potassium hydroxide solution. Neither could the rearrangement be effected by the action of phosphorus pentachloride, acetyl chloride in acetic anhydride solution, or hydrogen chloride in acetic acid.

Oxidation of the lactam (XIII) or (XIV) by perhydrol in glacial acetic acid gave the corresponding sulfone (XV) or (XVI).


(XV)


(XVI)

The lactam (XIII) or (XIV) was subjected to hydrolytic cleavage by boiling with hydrochloric acid and by treating the hydrochloride obtained, first with silver oxide and then with hydrogen sulfide, the acid (XVII) or (XVIII) was separated:



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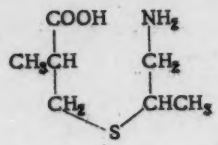
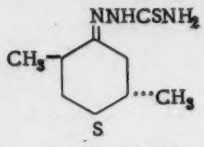


(XVIII)

In connection with the search for new medicinal preparations, it seemed of interest to prepare the thiosemicarbazones (XIX) and (XX), and also the semicarbazone (XXI), and to test them for antitubercular activity. These compounds were prepared by the usual method from the corresponding ketones:



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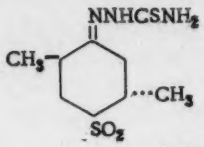
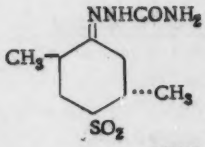


(XX)



(XXI)

The compounds (III), (IV), (VII), (X), (XII), (XIX), (XX), and (XXI) were tested for antibacterial activity and found to be slightly active.

EXPERIMENTAL

The trans isomer of 2,4-dimethyltetrahydro-1-thiopyran-4-one (I) with m.p. 71° and its corresponding sulfone (II) with m.p. 138° [4] were used as starting materials.

2,5-Dimethyltetrahydro-1-thiopyran-4-one oxime (III). A mixture of 20 g of thiopyrone (I) dissolved in 20 ml of alcohol and a solution of 14 g of hydroxylamine sulfate with 17 g of sodium acetate in 40 ml of water was heated to 100° for 6 hours. On cooling, crystals separated; these were washed with water and recrystallized from alcohol. Yield 18.1 g of oxime (III) as colorless needles with m.p. 131-132°.

	Found %:	C 52.82, 52.63;	H 8.23, 8.28;	S 20.13, 20.14.
$C_7H_{13}ONS$.	Calculated %:	C 52.77;	H 8.22;	S 20.12.

Oxime of dihydroxy 2,5-dimethyltetrahydrothiopyran-4-one (IV). A mixture of a solution of 10 g of the sulfone (II) in 20 ml of alcohol and a solution of hydroxylamine sulfate with 4.5 g of sodium acetate in 20 ml of water was heated to 100° for 6 hours. The crystals which separated on the following day were collected and recrystallized from alcohol. Yield 7.15 g of oxime (IV) as colorless needles with m.p. 194-195°.

	Found %:	C 44.15, 43.96;	H 6.81, 6.99;	S 16.53, 16.98.
$C_7H_{13}O_3NS$.	Calculated %:	C 43.94;	H 6.85;	S 16.76.

2,5-Dimethyltetrahydro-1-thiopyran-4-amine (VI). To a solution of 5.8 g of the oxime (III) in 80 ml of absolute alcohol heated to 40°, 14 g of sodium, in small pieces, was added over 45 minutes with constant stirring. The cooled solution was diluted with water (80 ml) and thoroughly extracted with ether (100 ml). The ethereal solution was shaken three times with 10% sulfuric acid (75 ml in all). The aqueous-acid solution was concentrated to 25 ml and made alkaline with 20% sodium hydroxide solution. The free base was thoroughly extracted with ether and dried over potash. The ether was carefully distilled off in a flask fitted with a long spiral column, and the residue was then distilled in a current of nitrogen. A yield of 2.9 g of 2,5-dimethyltetrahydro-1-thiopyran-4-amine (VI) was obtained; it had b.p. 213°, and solidified to form colorless crystals with m.p. 37-40°.

	Found %:	C 57.55, 57.53;	H 10.54, 10.66.
$C_7H_{15}NS$.	Calculated %:	C 57.85;	H 10.40.

The amine (VI) was very soluble in most organic solvents and in water; it readily absorbed atmospheric carbon dioxide, forming the carbonate with m.p. 104-114°. The latter was stable when stored, but on heating it decomposed to give the original amine. When dry hydrogen chloride was passed through an alcoholic solution of the amine (VI), the subsequent addition of dry ether precipitated the hydrochloride (VII) as fine needles with m.p. 256-257°. The hydrochloride was stable in air and very soluble in water.

Found %: Cl 20.08, 19.80.
$C_7H_{15}NSCl$. Calculated %: Cl 19.51.

0.2 g of the amine (VI) and 0.5 g of acetic anhydride were set aside in a stoppered flask for 24 hours. The crystals of the acetyl derivative which formed (VIII) were recrystallized from benzene; they melted at 190-191°.

Found %: N 7.63, 7.59.
$C_9H_{17}ONS$. Calculated %: N 7.51.

5 g of the carbonate of the amine (VI) was dissolved by the aid of heat in 40 ml of dry pyridine. To the cooled solution 10 g of freshly distilled benzoyl chloride was added. Heat was evolved and a copious crystalline precipitate formed immediately. The crystals were filtered off, washed with weak sodium carbonate solution, and recrystallized from benzene. A yield of 4 g of the benzoyl derivative (IX) in the form of colorless crystals with m.p. 182-183° was obtained.

Found %: N 5.95, 6.08.
$C_{14}H_{19}ONS$. Calculated %: N 5.69.

Oxidation of 2,5-dimethyltetrahydro-1-thiopyran-4-amine hydrochloride (VII) with perhydrol. a) To a solution of 0.2 g of amine hydrochloride (VII) in 30 ml of glacial acetic acid, 2.8 ml of 30% perhydrol was added. After three days the bulk of the acetic acid was distilled off under reduced pressure. The precipitate was filtered off (0.25 g) and washed with ether. The aminosulfone hydrochloride (X) was purified by dissolving in alcohol and precipitating with ether, after which it melted at 285-286° (with decomposition).

Found %: N 6.71, 6.68.
$C_7H_{16}O_2NSCl$. Calculated %: N 6.58.

b) To a solution of amine hydrochloride (VII) in 75 ml of glacial acetic acid, 7 ml of 17% perhydrol solution was added. After four days the bulk of the acetic acid was distilled off under reduced pressure. The aminosulfoxide hydrochloride (XI) (0.5 g) was filtered off and after recrystallization from alcohol it melted at 330°.

Found %: N 7.24, 7.22.
$C_7H_{16}ONSCl$. Calculated %: N 7.07.

Oxidation of the amine benzoyl derivative (IX) with perhydrol. To a solution of 2 g of the benzoyl derivative (IX) in 40 ml of glacial acetic acid, 4 ml of 17% perhydrol was added. After three days the acetic acid was distilled off under reduced pressure, and after dilution with water the residue crystallized. A yield of 2 g of the sulfone (XII) was obtained; after recrystallization from alcohol it melted at 286-287°.

Found %: N 5.30, 5.45.
$C_{14}H_{14}O_3NS$. Calculated %: N 5.00.

Action of alcoholic ammonia and metallic sodium on the thiopyrone (I). To a solution of 5 g of thiopyrone (I) in 25 ml of 10% ammonia in absolute alcohol, 6.5 g of metallic sodium and 35 ml of absolute alcohol were gradually added, with stirring. After all the sodium had been dissolved 50 ml of water was added to the reaction mass, and the product was extracted with ether (100 ml). The ethereal solution was shaken with 10% hydrochloric acid (100 ml). The acid solution was evaporated to dryness and the salts obtained were dried in a vacuum desiccator and recrystallized by dissolving in water and precipitating with ether. A yield of 0.9 g (14% of the theoretical) of amine hydrochloride (VII) with m.p. 256-257° was obtained. A mixed melting point with the sample described above showed no depression. In addition 2.5 g of the initial thiopyrone (I) with m.p. 70-71° was obtained.

Rearrangement of the oxime (III) under the influence of sulfuric acid. 5.8 g of the oxime (III) and 9 ml of sulfuric acid were heated to boiling in a porcelain dish. The reaction mixture was cooled and gradually poured into 45 ml of 20% aqueous potassium hydroxide solution cooled with ice-water. The product was extracted with chloroform. The solvent was removed by distillation and the residue recrystallized from water with the addition of animal charcoal. A yield of 3.7 g of crystals of the lactam (XIII) or (XIV) with m.p. 139-142° was obtained. After three recrystallizations from water, 1.8 g of pure substance melting at 149-150° was separated:

Found %: C 52.90, 53.05; H 8.44, 8.43; S 20.07, 19.92.
$C_7H_{13}ONS$. Calculated %: C 52.77; H 8.22; S 20.12.

Oxidation of the lactam (XIII) or (XIV) with perhydrol. To a solution of 0.9 g of the lactam (XIII) or (XIV) in 5 ml of glacial acetic acid, 1.4 ml of 28% hydrogen peroxide solution was added. After three days the acetic acid was distilled off under reduced pressure and the residue recrystallized from alcohol. A yield of 1 g of sulfone (XV) or (XVI) as colorless needles with m.p. 221° was obtained.

	Found %:	C 44.04, 44.12;	H 6.87, 7.09;	S 16.98, 16.85.
$C_7H_{13}O_3NS$.	Calculated %:	C 43.95;	H 6.85;	S 16.77.

Hydrolysis of the lactam (XIII) or (XIV). A solution of 0.5 g of the lactam (XIII) or (XIV) in 2 ml of 10% hydrochloric acid was heated to 80° for one hour. The solution was evaporated under reduced pressure, and 2 ml of water was added to the residue after which the solution was again evaporated. 2 ml of water and 1 g of silver oxide were added to the residue. The precipitated silver chloride was filtered off and washed with water; the wash waters were treated with hydrogen sulfide. The separated silver sulfide was filtered off and thoroughly washed with water; the filtrate and wash waters were evaporated under reduced pressure. The glassy residue was dissolved in alcohol and precipitated with ether. A yield of 0.4 g of thioaminoacid (XVII) or (XVIII), as colorless crystals with m.p. 183-184° was obtained:

	Found M:	185.2.		
	Calculated M:	177.33		
	Found %:	C 45.91, 46.16;	H 8.38, 8.51;	S 17.94, 18.03.
$C_7H_{15}O_2NS$.	Calculated %:	C 47.42;	H 8.53;	S 18.09.

Thiosemicarbazone of 2,5-dimethyltetrahydro-1-thiopyran-4-one (XIX). Thiosemicarbazide (0.9 g) was dissolved with the aid of heat on the water bath in 30 ml of water and 2 ml of glacial acetic acid. To the hot semicarbazide solution 1.4 g of thiopyrone (I) dissolved in 25 ml of absolute alcohol was added. The precipitate of thiosemicarbazone (XIX) which formed immediately was recrystallized from alcohol and then melted at 162-163°.

	Found %:	N 19.30, 19.39.
$C_8H_{15}N_3S_2$.	Calculated %:	N 19.41

Thiosemicarbazone of dihydroxy 2,5-dimethyltetrahydro-1-thiopyran-4-one (XX). Thiosemicarbazide (0.9 g) was dissolved with heating on the water bath in 30 ml of water and 3 ml of glacial acetic acid. The slightly cooled solution was poured into a solution of 1.7 g of the sulfone (II) in 25 ml of absolute alcohol. The liquid was heated on the water bath for 15 minutes. The thiosemicarbazone (XX) melted at 241° (from water).

	Found %:	N 16.67, 16.58.
$C_8H_{15}O_2N_3S_2$.	Calculated %:	N 16.92.

Semicarbazone of dihydroxy 2,5-dimethyltetrahydro-1-thiopyran-4-one (XXI). The semicarbazone (XXI) was obtained from the sulfone (II) in the usual manner; it consisted of colorless needles melting at 217-218° (from water):

	Found %:	N 18.54, 18.40.
$C_8H_{15}O_3N_3S$.	Calculated %:	N 18.10.

SUMMARY

1. By the interaction of 2,5-dimethyltetrahydro-1-thiopyran-4-one (I) and its corresponding sulfone (II) with hydroxylamine hydrochloride in alcoholic solution, the corresponding oximes (III) and (IV) were obtained.

2. Reduction of the oxime (III) with sodium in absolute alcohol afforded 2,5-dimethyltetrahydro-1-thiopyran-4-amine, which by analogy with compounds of the cyclohexane and piperidine series must have the trans-structure (VI). Attempts to prepare the second possible stereoisomer of the amine (V) by reducing the oxime (III) in an acid medium were not successful.

3. The same amine (VI) was obtained in 14% yield by the action of metallic sodium in alcoholic ammonia solution on the thiopyrone (I).

4. The hydrochloride (VII), the acetyl derivative (VIII), and the benzoyl derivative (IX) of the thiopyran amine, and also the hydrochloride (X) and the benzoyl derivative (XII) of the aminosulfone, and the hydrochloride of the aminosulfoxide (XI) have been prepared.

5. It is shown that the oxime of the tetrahydropyran series (III) rearranges to the lactam (XIII) or (XIV) on heating with sulfuric acid; hydrolytic cleavage of the lactam gave the thioamino acid (XVII) or (XVIII).

6. The thiosemicarbazones of 2,5-dimethyltetrahydro-1-thiopyran-4-one (XIX) and its corresponding sulfone (XX), and the semicarbazone of dihydroxy-2,5-dimethyltetrahydro-1-thiopyran-4-one (XXI) have been prepared.

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* See Consultants Bureau Translation, p. 897.

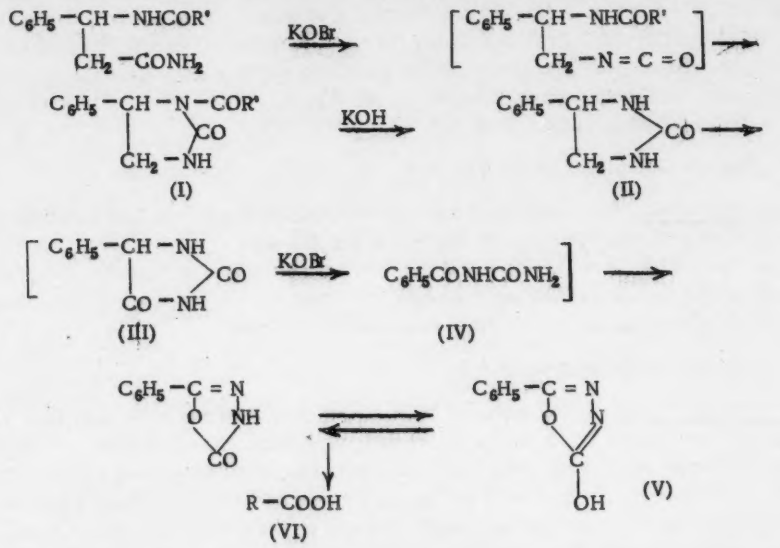
** See Consultants Bureau Translation, p. a-621.

NEW INFORMATION ON THE HOFMANN REACTION

COMMUNICATION 5. REACTION OF AMIDES OF N-ACYLATED β-PIPERONYL-β-ALANINES WITH ALKALINE HYPOBROMITES*

V.M. Rodionov and V.V. Kiseleva

In previous papers [1,2] we were able to show that the action of alkaline hypobromite solutions on amides of N-acylated β-phenyl-β-alanines proceeds in the following manner:



The substances (I) 1-N-acyl-5-phenylglyoxalidone, (II) 5-phenylglyoxalidone, (V) 5-phenyl-1,3,4-oxadiazol-2 (3H) -one and (VI) benzoic acid were separated from the reaction mixture, and the possibility of the formation of the substances (III) and (IV) (5-phenylhydantoin and acylurea) was shown in an indirect manner. Under the conditions of the Hofmann reaction, synthetically prepared phenylhydantoin and benzoylurea gave phenyloxadiazolone and benzoic acid. The mechanism given is a special case of a general mechanism for the reaction of hypobromites with amides of N-acylated β-aminoacids given by Rodionov and Zvorykina [3,4], where it is shown that in this reaction there is a difference in the further course of the process: 5-alkylglyoxalidones are oxidized to hydantoin derivatives and further, through α-ureidoacids to α-aminoacids; the alkyloxadiazolone could not be separated from the reaction mixture; 5-phenylglyoxalidone leads to the formation of 5-phenyloxadiazolone and benzoic acid through phenylhydantoin and benzoylurea which are not separated. Neither the α-ureido- or the α-aminoacid was separated from the alkaline medium.

In order to confirm the mechanism given on another representative of the β-aminoacids of the aromatic series, studies were carried out with amides of three acyl derivatives (benzoyl, acetyl and carbomethoxy) of β-piperonyl-β-alanine and it was shown that with these the reaction also proceeds by means of the mechanism given above; in all three cases 5-piperonylglyoxalidone (m.p.212-213°), 5-piperonyl-1,3,4-oxadiazol-2 (3H) -one (m.p. 242-243°) and piperonylic acid were separated; in the case of the benzoyl derivative, 1-N-benzoyl-5-piperonylglyoxalidone (m.p.255-256°) was also obtained. The latter gave no depression in a mixed melting point determination with 1-N-benzoyl-5-piperonylglyoxalidone (m.p. 241°) obtained by Rodionov and Bezinger [5] by carrying out the Curtius reaction on β-piperonyl-β-alanine.

* Communications 4, see our paper in this journal, 1951, p. 57.

The reaction was carried out under the conditions we used previously in our work with β-phenyl-β-alanine (8 moles of alkali as a 13% solution and 2 moles of bromine per mole of amide; heating to 80°), and also under the somewhat milder conditions used by Rodionov and Zvorykina in work with β-aminopellargonic acid (7.6 moles of alkali and 2 moles of bromine per mole ofamide; heating to only 65°). In the latter case, 1-N-benzoyl-5-piperonylglyoxalidone was easily separated and piperonylic acid only with difficulty.

5-Piperonyl-1,3,4-oxadiazol-2(3H)-one and piperonylic acid were separated from the amide of N-carbomethoxy-β-piperonyl-β-alanine; from the amide of N-acetyl-β-piperonyl-β-alanine a substance with m.p. 265-266°, containing bromine and having the elementary composition $C_{12}H_{13}O_4N_2Br$ was obtained. The structure of this compound has not yet been established.

EXPERIMENTAL

β-Piperonyl-β-alanine was obtained in 40% yield by the method of Rodionov [6] in 50% yield by the method of Johnson [7], and in 60% yield by the method of Johnson as modified by Rodionov and Kravchenko [8]. N-benzoyl-β-piperonyl-β-alanine was prepared by the usual method, as already described by Bezinger [5].

N-Acetyl-β-piperonyl-β-alanine. To 5 g of β-piperonyl-β-alanine in 40 ml of 10% potassium hydroxide solution 4.1 g (3.85 ml) of acetic anhydride was added dropwise with constant mechanical stirring over 45 min. at 17-25°. At the end of the reaction a further 1.5 ml of 40% alkali was added (to make reaction alkaline). Stirring was continued for a further two hours and the solution was gradually acidified with dilute hydrochloric acid (1:1). The precipitate formed was filtered off, washed with cold water and dried. Yield, 6 g, m.p. 184-186° (quantitative yield); after recrystallization from hot water obtained in needles with m.p. 189-190°.

Found %: N 5.65; 5.65; $C_{12}H_{13}O_5N$. Calculated %: N 5.58.

N-Carbomethoxy-β-piperonyl-β-alanine. To a solution of 5 g of β-piperonyl-β-alanine in 10% potassium hydroxide solution (4g of solid KOH) 2.1 ml of methyl chloroformate was added dropwise at -2 to +2° with mechanical stirring (10% excess). Stirring was contined for a further hour and the solution was then acidified with hydrochloric acid (1:1). The oil which separated crystallized on standing overnight. Yield of N-carbomethoxy-β-alanine with m.p. 134-136°, 3.9 g (61% of theory); m.p. after recrystallization from ethanol 137-138°.

Found %: N 5.25; 5.13; $C_{12}H_{13}O_6N$. Calculated %: N 5.24.

Amide of N-benzoyl-β-piperonyl-β-alanine. Thirty grams of N-benzoyl-β-piperonyl-β-alanine and 13.6 ml of thionyl chloride (twofold quantity) were heated to 40° on the water-bath for 4 hours. Absolute ether was added to the oil formed and heating was continued for an hour and a half. The solidified mass was washed several times with absolute ether, the ether being decanted; on rubbing with a glass rod the whole mass crystallized under the ether; it was shaken up with fresh portions of ether and the suspension obtained was saturated with dry ammonia (the ether portions used for washing were saturated separately). The precipitate obtained was filtered off, washed with ether and dried in air; it was then washed four times with alkali and with water. On acidification the alkaline solution gave 0.2 g of the starting N-benzoyl derivative of β-piperonyl-β-alanine. Weight of solid amide, 25.5 g; m.p. 262-263°; after recrystallization fron. ethanol the m.p. was 267-268°. The amide was insoluble in hot water and slightly soluble in hot alcohol.

Found %: N 9.16; 9.31; $C_{17}H_{16}O_4N_2$. Calculated %: N 8.97.

The ethereal solution obtained in washing the reaction mass yielded a further 1.5 g of amide. Total yield of amide, 27 g (90% of theory).

Amide of N-acetyl-β-piperonyl-β-alanine. Twenty grams of N-acetyl-β-piperonyl-β-alanine and 17 ml of thionyl chloride (three times the theoretical quantity) were heated to 40° for two hours. Because the oil obtained was insoluble in both absolute benzene and absolute alcohol, it was treated several times with absolute ether, which was decanted. The solidified oil was rapidly rubbed in a mortar, shaken with ether and saturated with ammonia with frequent shaking (the ether from the washing was saturated separately). The solid was filtered off, dried in air, and washed with alkali and water. A yield of 14.8 g of amide with m.p. 200-201° was obtained; acidification of the alkaline solution gave 3.2 g of the starting N-acetyl-β-piperonyl-β-alanine. Yield of recrystallized amide, 88%. The amide was soluble in hot water and in hot alcohol. After two recrystallizations from hot water the m.p. was 213-214°.

Found %: N 11.20, 11.26; $C_{12}H_{14}O_4N_2$. Calculated %: N 11.20.

Amide of N-carbomethoxy-β-piperonyl-β-alanine. Twenty grams of N-carbomethoxy-β-piperonyl-β-alanine was heated with 10 ml of thionyl chloride (twice the theoretical) at 40° for two hours. The excess thionyl chloride was removed from the dark oil thus obtained by distillation under reduced pressure; and absolute ether was added to the oily residue. A suspension of the crystallized mass in ether was saturated with dry ammonia, with cooling and frequent shaking. The residue was filtered off, dried in air and washed three times with alkali and water. Yield of the recrystallized product with m.p. 212-216°, 16 g (~80% of theory). The amide was sparingly soluble in hot water and in hot alcohol. Yield of amide recrystallized from alcohol, 70%; m.p. 225-226°.

Found %: N 10.48; 10.62; $C_{12}H_{14}O_5N_2$. Calculated %: N 10.53.

The yield was lower when the theoretical amount of thionyl chloride was used.

Hofmann Reaction with the amide of N-benzoyl-β-piperonyl-β-alanine. (7.6 moles of KOH and 2 moles of bromine per mole of amide; heating to only 65°).

To 13% potassium hydroxide solution, containing 13.6 g of solid KOH, 3.3 ml of bromine was added at a temperature of −12-10°, and then 10 g of amide was added over two hours with stirring. The stirring was continued for a further hour in the cold and then for half-an-hour at room temperature The temperature of the bath was raised to 30°, when the amide dissolved completely. The heating was continued and at 50° the flask was removed from the bath, but the temperature inside the mixture rose spontaneously to 63°, while a solid separated and bubbles of gas were evolved. The flask was rapidly cooled, the precipitated solid filtered off and washed with acid, with water, with alkali and finally again with water. When made alkaline, the acid gave 0.2 g of a substance with m.p. 210-212° (I) and a residue of 4.3 g with m.p. 190-193° (II). The solution was extracted with ether during the extraction 0.3 g of the original amide separated. As a result of step-wise treatment of the solution with hydrochloric acid (1:1), two substances were separated:

Substance (III), 2.3 g; m.p. 183 to 215°.

Substance (IV), 2.05 g; m.p. 105-110°.

After purification of these four substances, the following were obtained:

1) 2.6 g of the starting amide,

2) 1.5 g of benzoic acid;

3) 0.1 g of N-benzoyl-β-piperonyl-β-alanine;

4) 2.4 g of 5-piperonylglyoxalidone (m.p. 212-213°).

Found %: C 58.26, 58.39; H 5.04, 4.97; N 13.36, 13.40. $C_{10}H_{10}O_3N_2$. Calculated %: C 58.25; H 4.85; N 13.59.

5) 0.3 g of 1-N-benzoyl-5-piperonylglyoxalidone - colorless needles with m.p. 255-256°; a mixed sample with the the original amide had m.p. 241-243°.

Found %: C 65.62; 65.76; H 4.70; 4.58; N 8.84; 8.87; $C_{17}H_{14}O_4N_2$ Calculated %: C 65.81; H 4.52; N 9.03.

6) 0.4 g of 5-piperonyl-1,3,4-oxadiazol-2(3H)-one - colorless needles with m.p. 243-244° (separted from other acids by treatment with bicarbonate).

Found %: C 52.43; 52.55; H 2.87; 2.93; N 13.62; 13.71; $C_9H_6O_4N_2$. Calculated %: C 52.43; H 2.91; N 13.59.

The structure of the 5-piperonyl-1,3,4-oxadiazol-2(3H)-one was confirmed by an alternative synthesis in which piperonylic acid hydrazide was treated with phosgene (method of Lieser and Nischk [9]. A mixed melting point on this product (m.p. 242-243°) and the product of the Hofmann reaction showed no depression.

Saponification of 1-N-benzoyl-5-piperonylglyoxalidone. 1-N-benzoyl-5-piperonylglyoxalidone (0.12 g) (m.p. 253-255°) was boiled for two hours on the water-bath with 20% KOH (with this treatment the turbid precipitate settled to the bottom and changed its form). After cooling, the solid was filtered off, washed with water and dried; 0.6 g of material with m.p., 208-209° was obtained, and a mixed melting point with 5-piperonylglyoxalidone gave no depression. On acidification and extraction with ether, the solution afforded 0.03 g of benzoic acid with m.p. 121-122°.

Hofmann Reaction with the amide of N-benzoyl-β-piperonyl-β-alanine under the earlier conditions. (8 moles of KOH 2 moles of bromine, heating to 80°).

This experiment differed from the prededing one in that after the temperature had increased the reaction mixture cooled and the solid separated, the solution was again heated to 55°. A further rise of temperature was observed;

the mixture was cooled and after separation of the precipitate, the solution was heated in two further steps: to 65 and to 80°. After removal of the precipitates, the solution was acidified as in the previous experiment. The products separated were worked up in the same way. The following were obtained from 10 g of amide:

1) 1.4 g of the original amide (m.p. 260°);

2) 1.2 g of pure 5-piperonylglyoxalidone (m.p. 212°)

3) 1.7 g of a mixture melting at 200-205° (not separated);

4) 0.08 g of 1-N-benzoyl-5-piperonylglyoxalidone (m.p. 253-255°).

5) 0.6 g of 5-piperonyl-1,3,4oxadiazol-2(3H)-one (m.p. 242-243°).

6) 2 g of benzoic acid (m.p. 120-121°);

7) 0.05 g of piperonylic acid (m.p. 230°) and

8) 0.05 g of N-benzoyl-β-piperonyl-β-alanine (m.p. 195°).

Hofmann Reaction with the amide of N-acetyl-β-piperonyl-β-alanine (7.6 moles of KOH, 2 moles of bromine, heating to only 65°)

To a solution of hypobromite, cooled to −12° and containing 17 g of solid KOH, 113 ml of water and 4.08 ml of bromine, 10 g of amide (m.p. 213°) was added with stirring over an hour and a half. The solution was heated on the water-bath to 50°; the flask was then removed from the bath, when the temperature spontaneously rose to 65° and cloudiness developed. The flask was placed in a cooling-mixture; the precipitate (3.15 g) was found to be 5-piperonylglyoxalidone (m.p. 213°). The solution was then carefully acidified in the usual manner with hydrochloric acid (1:1) and the products separated were purified. From 10 g of amide the following were obtained:

1) 2.1 g of original amide (recovered);

2) 3.15 g of 5-piperonylglyoxalidone;

3) 0.7 g of 5-piperonyl-1,3,4-oxadiazol-2-(3H)-one;

4) 0.05 g of piperonylic acid and

5) 0.15 g of a bromine-containing substance having the elementary composition $C_{12}H_{13}O_4N_2Br$.
Found %: C 43.78, 43.72; H 4.12, 4.04; N 8.31, 8.10. $C_{12}H_{13}O_4N_2Br$. Calculated %: C 43.77; H 3.95; N 8.51.
The examination of this substance has not yet been completed.

When the Hofmann reaction was carried out on N-acetyl-β-piperonyl-β-alanine with heating to 80°, the main reaction product obtained in three experiments was 5-piperonylglyoxalidone (yield 70-75%, based on the unrecrystallized product with m.p. 206-210°). In addition small amounts of 5-piperonyl-1,3,4oxadiazol-2(3H)-one, N-acetyl-β-piperonyl-β-alanine and piperonylic acid were separated, as negligible quantities (0.03 g from 10 g of amide) of a bromine-containing compound, $C_{12}H_{13}O_4N_2Br$. The amide taken was entirely consumed in the reaction.

Hofmann Reaction with the amide of N-carbomethoxy-β-piperonyl-β-alanine.

This was carried out also under both mild and extreme conditions. From 10 g of amide the following were obtained:

Heating to 65°	Heating to 80°
3.5 g of original amide	0.1 g of originial amide
1.2 g of 5-piperonylglyoxalidone	4 g of pure 5-piperonylglyoxalidone (yield 51%; yield of technical product, 70%)
0.5 g of a mixture of 5-piperonylglyoxalidone and amide (m.p. 202-203°)	0.7 g of a mixture of 5-piperonyl-glyoxalidone and the amide
0.65 g of 5-piperonyl-1,3,4-oxadiazol-2-(3H)-one	1 g of 5-piperonyl-1,3,4-oxadiazol-2-(3H)-one
0.05 g of piperonylic acid	0.05 g of piperonylic acid

Subsequent experiments differed from the preceding ones in that the amide of the N-carbomethoxy derivative, which is difficult to wet, was first suspended in water and the hypobromite solution (calculated to make the alkali concentration 13%) was added dropwise to the suspension.

SUMMARY

1. The Hofmann Reaction has been carried out with the amides of N-benzoyl, N-acetyl and N-carbomethoxy- β-piperonyl-β-alanine under different conditions (heating to 65° and 80°).

2. It has been shown that in all cases the reaction mechanism is the same as that which occurs with the amides of of N-acylated β-phenyl-β-alanines. The mechanism may be considered a general one for amides of N-acylated aminoacids of the aromatic series. *

3. In all three cases 5-piperonylglyoxalidone, 5-piperonyl-1,3,4-oxadiazol-2(3H)-one and piperonylic acid were separated from the reaction-mixture; in addition the reaction with N-benzoyl-β-piperonyl-β-alanine yielded 1-N-benzoyl-5-piperonylglyoxalidone.

4. It has been shown that the separation of 1-N-benzoyl-5-piperonylglyoxalidone takes place readily under the conditions used by Rodionov and Zvorykina for amino-acids if the aliphatic series (heating to 65°), and the separation of piperonylic acid under the more drastic conditions (heating to 80°) which we have previously used (reaction proceeding further).

5. When the Hofmann Reaction was carried out on N-acetyl-β-piperonyl-β-alanine, a bromine-containing compound of composition $C_{12}H_{13}O_4N_2Br$ was separated.

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* The formation of 1-N-acyl-5-arylglyoxalidone and 5-arylglyoxalidone has already been confirmed for β-(α-naphthyl)-β-alanine by V.M. Rodionov and N. A. Kravchenko [8].

** See Consultants Bureau Translation, p. 847.

STUDY OF THE REACTION MECHANISM OF CYCLIZATION WITH THE AID OF DEUTERIUM

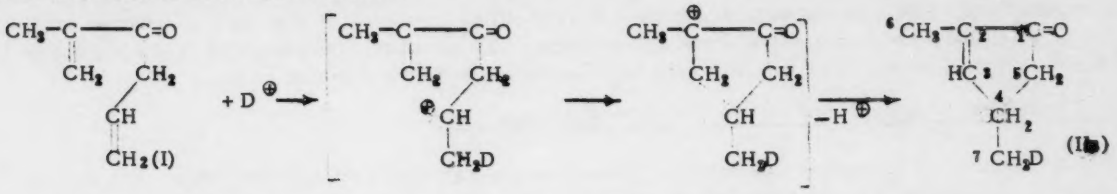
COMMUNICATION 2

I. N. Nazarov, I. I. Zaretskaya, Z. N. Parnes, and D. N. Kursanov

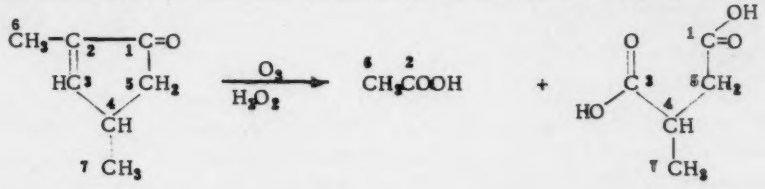
In a previous paper [1] we showed that the cyclization of 2-methylhexadien-3-one in the presence of deuterium-enriched phosphoric acid results in the introduction of deuterium into the molecule of dimethylcyclopentenone formed. From this observation it unambiguously follows that the cyclization reaction of this ketone proceeds by way of the intermolecular ionic mechanism proposed by Nazarov [2].

The aim of the present work was to determine the position into which the deuterium from deuterium-enriched phosphoric acid was introduced into the molecule of dimethylcyclopentenone formed. The determination of this position would make it possible to decide the question of the structure of the dienone entering this cyclization reaction. In order to solve this problem, we carried out the cyclization of 2-methylhexadien-3-one with the aid of deuterium-enriched phosphoric acid.

The combustion water thus obtained from dimethylcyclopentenone had an excess density equal to 2730 γ In this case, if the dienone entering the reaction had structure (I). then, as the scheme shown below demonstrates, the deuterium should be found at carbon 7.



In order to locate the deuterium, we ozonized the deuterium-containing dimethylcyclopentenone. As a result of this treatment and subsequent oxidation with hydrogen peroxide, methyl succinic acid was obtained having about the same amount of deuterium enrichment as the original dimethylcyclopentenone. On igniting this methyl succinic acid. water having an excess density of 2760 γ instead of the calculated 3410 γ was obtained. From this it follows that the deuterium could only be located at the carbon atoms 4, 5, or 7.

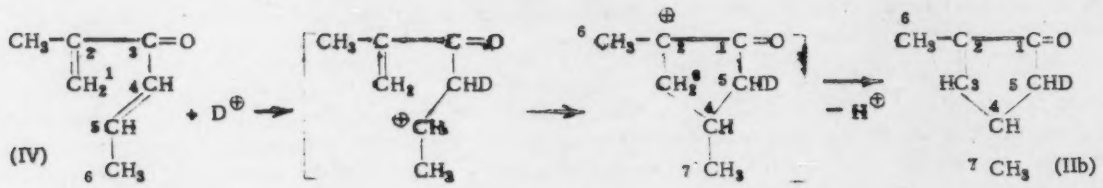


Further, the detuerium-containing dimethylcyclopentenone was subjected to oxidation with selenium dioxide. On oxidation of dimethylcyclopentenone, as was shown by Nazarov and Torgov [3], dimethylcyclopentendione is formed according to the following scheme:

If the deuterium occurred in the methyl group (formula IIa) the deuterium content of the diketone (III) should be the same as that of the initial dimethylcyclopentenone. However, it was found in fact that the diketone (III)

contained practically no deuterium. The combustion water of the diketone (III) had a density excess of 94 γ instead of the calculated 3410 γ.* Thus it was shown that the oxidation of dimethylcyclopentenone (II) to dimethylcyclopentedione (III) is connected with the removal of deuterium.

Since the diketone (III) differs from the ketone (II) by the absence of hydrogen atoms at carbon 5, the absence of deuterium in the diketone (III) means that the deuterium in dimethylcyclopentenone is in the methyl group of carbon 5 (formula IIb). The fact that deuterium, as a result of the cyclization reaction, adds at carbon 5 may be explained only by supposing that the cyclization is actually undergone not by isopropenylallylketone (2-methyl-1,5-hexadien-3-one)(I), but by its isomer, 2-methyl-1,4-hexadien-3-one, (IV). In this case the reaction follows the following mechanism:



EXPERIMENTAL

Deuterodimethylcyclopentenone was obtained by cyclizing 2-methylhexadien-3-one with deuterium-enriched phosphoric acid. Before the experiments the dienone was distilled on a colum with a single glass-wound spiral having an efficiency of 25 theoretical plates and equipped with a manostat. The phosphoric acid was prepared from phosphoric anhydride and deuterium-enriched water containing about 50% of deuterium oxide.

Preparation of deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one (IIb)

Experiment 1. In a 3-necked flask equipped with a stirrer, a dropping funnel and thermometer, 21.9 g of 2-methylhexadien-3-one (b.p. 68.5 -69.0° at 35 mm, $n_D^{20.4}$ 1.4732) was placed and phosphoric acid was gradually added with stirring and cooling by means of ice water. The phosphoric acid was obtained from 23.9 g of phosphoric anhydride and 7.8 g of deuterium-enriched water containing ~50% of deuterium oxide. During this operation the temperature in the reaction flask was maintained at 5-10°. After addition of phosphoric acid, the reaction mixture was stirred for a further 7 hours at 20°. The product was neutralized by sodium bicarbonate solution, extracted with ether, dried over sodium sulphate and, after removal of the ether, distilled under reduced pressure. Two fractions were obtained:

Fraction 1) b.p. 75-90° at 42 mm, 8.8 g.
Fraction 2) b.p. 90-100° at 42 mm, 2.1 g.

Fraction 1 was redistilled under diminished pressure and 6.5 g of ketone (IIb) with boiling point 75-76° at 30 mm; n_D^{20} 1.4670 was obtained. One gram of this substance was examined for deuterium. The water was burned in the usual laboratory apparatus and its density measured by the fusion method. The excess density of the combustion water was 2960 γ.

Experiment 2. 42.1 g of 2-methylhexadien-3-one (b.p. 57.5-58°) at 21 mm; n_D^{20} 1.4730) was subjected to the cyclization reaction in the presence of deuterium-enriched phosphoric acid obtained from 33.1 g of phosphoric anhydride and 16.3 g of water containing ~50% of deuterium oxide.

The reaction was carried out for 4 hours at 20° as described in the previous experiment. On distillation under reduced pressure at 11 mm the following fractions were obtained:

Fraction 1, b.p. to 57.0°; n_D^{21} 1.4660 – 0.4 g;

Fraction 2, b.p. 57.0-59.5°; n_D^{21} 1.4672 – 17.7 g;

Fraction 3, b.p. 60.0-83.0°; n_D^{21} 1.4642; – 4.3 g.

* In order to find if the oxidation was accompanied by deuterium exchange, we carried out an oxidation experiment on light dimethylcyclopentenone with selenium dioxide in deuterium-containing acetic acid. It was found that the diketone obtained did not contain deuterium. This shows that there is no deuterium exchange under experimental conditions.

Fraction 2 consisted of dimethylcyclopentenone (II b). The excess density of the combustion water was 2730 γ (in the combustion 2.1 g of the dimethylcyclopentenone was used)

Ozonization of Deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one (IIb)

To a solution of 5 g deuterodimethylcyclopentenone obtained in Experiment 2, in 35 g of carbon tetrachloride, ozonized oxygen was passed for 8 hours at the rate of 3-4 litres per hour (ozone concentration 6%). The ozonized solution was poured into 25 ml of 5% hydrogen peroxide and mixed for 4 hours at 50°. The carbon tetrachloride and volatile acids were distilled off under slightly reduced pressure. The residue, in the form of a thick syrupy liquid, crystallized on cooling with an ice-salt mixture. The crystals (1.2 g) were filtered off and washed with cold ether, when they melted at 105-107°. After recrystallization from a benzene-light petroleum mixture, 0.4 g of crystals with m.p. 107-109° was obtained. The crystals were dried for four hours at a temperature of 70° under a pressure of 1 mm, after which they melted at 109-111° and gave no depression with a mixture of authentic methyl succinic acid. The volatile acids were neutralized with soda, the aqueous solution of salts evaporated to dryness and the salts treated with concentrated hydrochloric acid; the organic acids were all thoroughly extracted with ether. After the ether was distilled off, 1.2 g of acetic acid with b.p. 105-110° was obtained. The residue of 1.2 g crystallized. The crystals on filtering off and washing with cold ether melted at 107-109° and did not give a depression with an authentic specimen of methyl succinic acid.

The methyl succinic acid obtained as a result of recrystallization with m.p. 109-111° was examined for deuterium. It was found that the combustion water had an excess density of 2760 γ instead of the calculated 3410 γ. For the combustion 0.35 g of methyl succinic acid was used. Thus the methyl succinic acid contained almost all the deuterium taken for the ozonization of deuterodimethylcyclopentenone.

Oxidation of Deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one to 2,4-dimethyl-Δ^2-cyclopenten-1,5-dione (III)

5.5 g deuterodimethylcyclopentenone from Expt. 1, 7 g glacial acetic acid, and 5.7 g finely ground selenium dioxide were heated under an air condenser on Wood's alloy at 95-100°. An exothermic reaction set in and continued for 15 minutes. The mixture was heated to 115-120° for 15 minutes more, and after cooling was diluted with 30 ml ether, filtered, the acetic acid distilled off under slightly reduced pressure, and the residue distilled under the reduced pressure of an oil-pump. The substance obtained, 1.6 g with b.p. 80-85° at 3 mm, solidified to form a dense orange to yellow crystalline mass. Recrystallization from a mixture of petroleum ether and benzene afforded 0.9 g of dimethylcyclopentendione (III) as well-formed golden crystals with m.p. 64-65°.

The deuterium content of this diketone was measured. The excess density of the combustion water was 240 γ instead if the calculated 3700 γ. One gram of the compound was used in the combustion. As is evident from the results, the diketone contained practically no deuterium.

In another experiment 10 g of deuterodimethylcyclopentenone, obtained in experiment 2, was oxidized with 11.3 g of selenium dioxide and 18 g of glacial acetic acid. The reaction was carried out under similar conditions to those described above, and 3.6 g of crystalline diketone was obtained. After recrystallization from mixed petroleum ether and benzene, 1.4 g of pure dimethylcyclopentendione with m.p. 66-67.5° was obtained. The excess density of the combustion water from this diketone was found to be 94 γ instead of the calculated 3410 γ. For the combustion 0.85 g of the diketone was used.

In order to meet the objection that an exchange of hydrogen atoms between the ketone and glacial acetic acid might possible occur during the oxidation of dimethylcyclopentenone to dimethylocyclopentendione, we carried out an experiment to study the possibility of this exchange. Ordinary dimethylcyclopentenone was oxidized with selenium dioxide in glacial acetic acid containing deuterium. In the experiment 9 g of ketone, 11.0 g of selenium dioxide and 14.7 g of glacial acetic acid, enriched in the carboxyl group to the extent of 40,000 γ, were used. The experiment was carried out as described above. A yield of 2.4 g of diketone with mp. 67-68° was obtained. The combustion water from the diketone had an excess density of 30 γ instead of the calculated 3800 γ for 1H, and 11,870 γ for 8 H.

It may therefore be considered as proved that the deuterium in 2,4-dimethyl-Δ^2-cyclopenten-1-one is practically entirely in the methylene radical α to the carboxyl group. The experimental results are given in the Table.

Substance	Excess density of of combustion water in γ	No. of H atoms in the molecule	Degree of "heaviness".	
			in γ	in % of D content of dimethylcyclopentenone
Dimethylcyclopentenone	2960	10	29 600	100
Dimethylcyclopentendione	240	8	1 920	6
Dimethycyclopentenone	2730	10	27 300	100
Methylsuccinic acid	2760	8	22 080	81
Dimethylcyclopentendione	94	8	750	3

SUMMARY

1. Deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one was obtained by the cyclization of 2-methylhexadien-3-one in the presence of deuterium enriched phosphoric acid.

2. When deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one was ozonized, methylsuccinic acid was obtained which contained almost all the initial deuterium of the dimethylcyclopentenone. This excludes the presence of deuterium at carbon atoms 1,2,3 or 6 in the molecule of deutero-2,4-dimethyl- Δ^2- cyclopenten-1-one.

3. Oxidation of deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one with seleniumdioxide gave 2,4-dimethyl--cyclopenten-1,5-dione containing no deuterium. From this it follows that the deuterium in deutero-2,4-dimethyl- Δ^2 -cyclopenten-1-one occurs at carbon 5, i.e., at the methylene group adjacent to the carbonyl.

4. This position of deuterium in deutero-2,4-dimethyl- Δ^2-cyclopentenone shows that it is not isopropenylallyl-ketone (2-methyl-1,5-hexadien-3-one) (I) but its isomer, 2-methyl-1,4-hexadien-3-one (IV) that is cyclized.

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[2] I.N. Nazarov, Prog. Chem., 20, 71 (1951).

[3] I.N. Nazarov and I. V. Torgov, J. Gen. Chem. 19, 1766 (1949);** Bull. Acad. Sci. USSR, Div. Chem. Sci. No.4, 417 (1951).

* See Consultants Bureau Translation, p. 103.

** See Consultants Bureau Translation, p. a-211.

PROGRESS IN RESEARCH ON THE CHEMISTRY OF ALKALOIDS OF ANABASIS APHYLLA*

A.S. Sadykov

In 1929 Orekhov, in studying the Central Asian plant Anabasis aphylla discovered a new liquid alkaloid of the composition $C_{10}H_{14}N_2$ (isomer of nicotine) and called it anabasine. In cooperation with Menshikov [2] the structure of anabasine was elucidated (α-piperidyl-β-pyridine) and from the plant new alkaloids were separated: lupinine $C_{10}H_{19}NO$, aphillidine, $C_{15}H_{22}N_2O$, aphilline, $C_{15}H_{24}N_2O$, and "base Y".

Anabasine was the first alkaloid discovered in the Soviet Union and served as the beginning of a large amount of work carried out by Orekhov, Menshikov and their co-workers on the study of the native flora. Soon after the discovery of anabasine, it was established that it had valuable insecticidal properties, and its industrial production from the plant (A aphylla) in the form of anabasine sulfate was begun. Anabasine sulfate is widely used as an agent for combatting agricultural crop pests, especially those affecting the cotton plant.

One of the most important branches of the national economy of our Republic is cotton raising. The Stalin program for the further increase in cotton productivity in the Uzbek. S.S.R., the main cotton base of our Union, stipulates an increase in the rate of growth of this branch of the agricultural industry hitherto unknown in world practice. The Directives of the 19th Congress of the Party on the 5th five-year Plan for the development of the U.S.S.R. call for an increase in the value of the harvest of raw cotton by 55-65% and an increase in the productivity of cotton in the regions of Central Asia to 26-27 centners per hectare.

In the Directives of the 19th Party Congress it is prescribed "To stipulate an increase in production capacity for ammonia, sulfuric acid, synthetic rubber, synthetic alcohol, soda, mineral fertilizers, especially the granulated types, and chemical agents for combatting plant pests"** The 11th Congress of the Communist Party of Uzbekistan called on the scientific research institutes in the Republic to develop more effective methods for countering pests and diseases of the cotton plant.

With these problems in mind we have in recent years carried out work on the chemical study of different types of anabasis for the content of alklaoids and other substances. At the same time we have made an extensive study of the chemistry of alkaloids of Anabasis aphylla with the object of modifying their molecules to obtain various pharmaceutical chemicals.

In the present article we give the results obtained by the author and his co-workers working in the Department of Plant Chemistry of the Central Asian State University (S.A.G.U.) and in the Institute of Chemistry of the Academy of Sciences, Uzbek. S S R.

There are about 30 species of anabasis in Central Asia. We have chemically examined [3] about ten species for their content of alkaloids, organic acids and other materials. As a result of work carried out in cooperation with the S.A.G.U. Ust-Urtsk expedition and especially with the Botanical Plant Institute of the Turkmenian Academy of Sciences [4, 5] considerable growths of A aphylla have been discovered in the region of the Central Turkmenian Canal and these were found to be richer in alkaloids than the plants from South Kazakhstan, which were being worked for anabasine sulfate. This cooperative work showed that it was possible to utilize a new raw material in industry and enabled the resources for the production of anabasine sulfate to be enlarged.

A chemical study of the plant [2] showed that A.aphylla contains a considerable amount of alkaloids from 1.29 to 12% (according to the data of various authors). The product was separated into two fractions by fractional distillation under reduced pressure. A low-boiling fraction (boiling point 136 to 138° at 2 mm), amounts to ~85% of the starting-material and a high-boiling fraction (boiling point ~200° at 2 mm) to 2.15%. The low-boiling fraction was separated by benzoylation or nitrosation and, as well as anabasine, a crystalline alkaloids, lupinine, $C_{10}H_{19}NO$,

* Report to the combined session of the Division of Chemical Sciences, Academy of Sciences, U.S.S.R., and the Academy of Sciences, Uzbek. S.S.R., 15.10.1952, Tashkent.

** Directives of the 19th Party Congress on the 5th five-year Plan for the development of the U.S.S.R., in 1951 to 1955. Pravda Press, 1952, page 10.

was obtained. From the high-boiling alkaloids the authors, making use of their different basicities, separated the crystalline alkaloids aphilline $C_{15}H_{24}N_2O$, aphillidine, $C_{15}H_{22}N_2O$, and "base V".

Because anabasine has powerful pharmacological properties, it can be used directly as a therapeutic agent. However, it is known that several of its derivatives (N-methylanabasine) have interesting physiological properties. In view of this and bearing in mind the ready availability of anabasine and other alkaloids of A. aphylla, we carried out various chemical operations on the base.

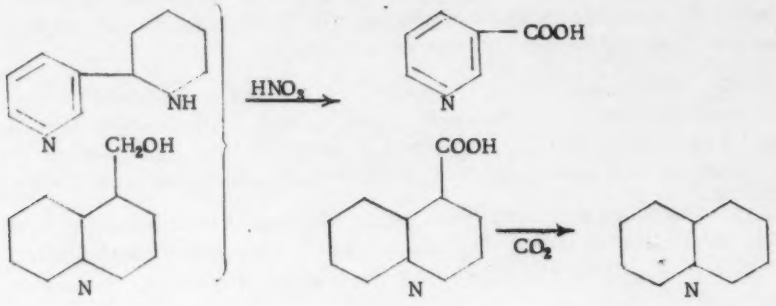
Before commencing this work it was necessary to develop methods for the separation of anabasine and other alkaloids of A. aphylla. For the separation of low-boiling alkaloids, apart from the methods of benzoylation and nitrosation mentioned above, other methods are used. Sokolov [6] proposed a fluosilicate method for the preparation of anabasine. Zaboev developed a new method in which nitrosation was carried out in acetic acid solution [7].

We have developed several new methods for separating anabasine or lupinine from mixtures of the two alkaloids [8]. Among these the hydrochloride method (formation of hydrochloride by the interaction of anabasine with hydrogen chloride or with ammonium chloride in acetone solution) is the simplest and the easiest and it may be recommended for the industrial preparation of pure anabasine. With a sufficient quantity of anabasine and the other alkaloids of A. aphylla at our disposal we were able to turn our attention to the chemical conversion of these bases.

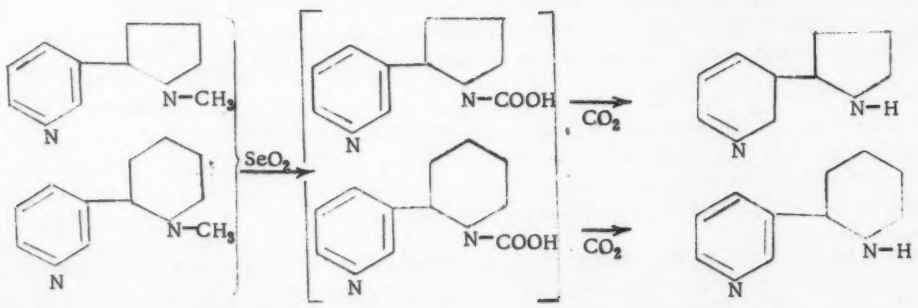
1. Oxidation of Anabasine.

As has been shown by Orekhov and Menshikov [2], when anabasine is oxidized with potassium permanganate, nicotinic acid is formed. This, apart from its use as the vitamin factor, is a raw material for a variety of further syntheses. We studied the oxidation of anabasine and its derivatives with different oxidizing agents in order to obtain nicotinic acid in large quantities for the needs of the medical institutions of our Republic.

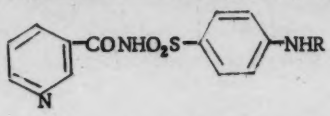
The oxidation of an anabasine-lupinine mixture with nitric acid [9] led to the formation of lupininic acid together with nicotinic acid. The former decarboxylizes with the formation of norlupinane:



The oxidation of cyclic and heterocyclic compounds has been studied by numerous workers. In review articles Melnikov [10] and Maior [11] have described numerous reactions of organic substances with selenium dioxide. Rodionov and his co-workers [12], studying the reaction in which cyclic and heterocyclic side chains are oxidized, developed an elegant and refined method for the preparation of the corresponding aldehydes. We [13] have oxidized anabasine, N-methylanabasine, and nicotine with selenium dioxide. Anabasine was found to be the most resistant to this oxidation and N-methylanabasine and nicotine oxidized forming the nor bases (anabasine and nornicotine):



In the literature there are many references to the synthesis of physiologically active compounds of nitotinic acid. We [14] have synthesized a number of new nicotinic acid derivatives mainly with several sulfanilamides. The general formula of the compounds obtained may be represented as follows:



Contrary to the findings of Daniels and Iwamoto [15], when sulfanilamide and nitotinyl chloride interact the main product is N-nicotinylsulfanilamide. Thus, by this synthesis we succeeded in solving the moot question in the literature on the addition of nicotinyl (the nicotinic acid residue) to the corresponding sulfanilamide group.

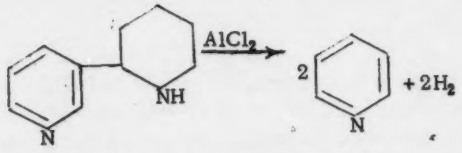
2. Fission of Anabasine

A number of workers have attempted to prepare pyridine from anabasine. Chelintsev and Dubinin [16] and later Aliev and Khanlarov [17] oxidized anabasine with nitric acid to nicotinic acid. By decarboxylation of the latter in the presence of a catalyst, pyridine was obtained. Dubinin and Chelintsev [18] subjected anabasine to pyrolysis on carbon at 580 to 600°. Pyridine was among the many products detected.

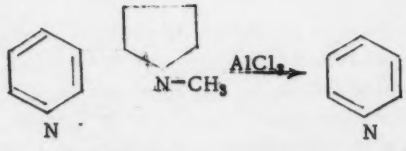
We have effected the fission of anabasine both thermally and by means of chemical reagents [19]. The thermal fission of anabasine (passing it through a heated quartz tube filled with activated clay or through an iron tube) yielded practically no pyridine. Of the chemical reagents for carrying out the fission of anabasine, zinc chloride, aluminum chloride, soda lime and metallic sodium were tried. We obtained good results with aluminum chloride and with metallic sodium.

It has been shown by various workers, especially by Zelinsky [20], that when aluminum chloride reacts with cyclic compounds the latter are dehydrogenated with the formation of various hydrocarbons.

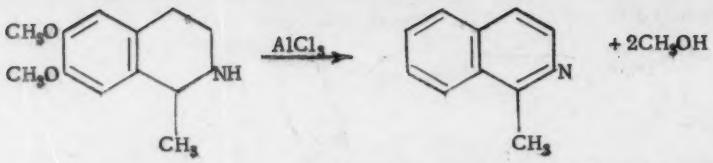
A series of reactions was carried out in which aluminum chloride acted directly on anabasine and on anabasine-lupinine mixtures. A yield of pyridine of 60-65% was obtained. The remainder of the anabasine was always recovered in the unchanged state. The absence of other reaction products prompted us to carry out some supplementary studies to establish the nature of the change of the piperidine nucleus in anabasine. Studying the reaction of piperidine with aluminum chloride under similar conditions, we were able to show that piperidine undergoes dehydrogenation with the almost quantitative formation of pyridine (yield 80-90%). Consequently, under the action of aluminum chloride the anabasine molecule suffers degradative fission at the $>C-C<$ (H) -bond with simultaneous dehydrogenation and the formation of two-pyridine molecules.



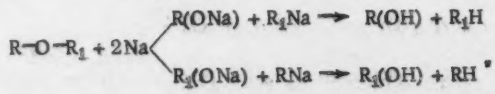
This was confirmed by subjecting nicotine to fission under similar conditions, when pyridine was obtained, but in a much smaller yield (12-15%). We were not able to observe in the reaction products even traces of pyrrole or pyrrolidine, since the latter under the reaction conditions evidently suffers profound changes.



The reaction of quinoline and of isoquinoline with aluminum chloride was then studied and it was shown that they are stable to this reagent. The alkaloid salsolidine (a derivative of tetrahydroisoquinoline) under these conditions gave 1-methylisoquinoline.



Metallic sodium was first proposed by Shorygin [21] for the cleavage of ethers and he proposed the following reaction mechanism:



However, we were not able to find in the literature any data relating to the cleaving action of metallic sodium on the $\geqslant C-CH<$ bond in heterocyclic compounds. When anabasine and metallic sodium were heated in molecular proportions (temperature 130-140°) destructive fission of anabasine takes place with the formation of pyridine (yield 70-75%). The pyridine formed was directly distilled from the reaction mixture. Thus, of chemical reagents, aluminum chloride and metallic sodium are recommended for the degradative fission of anabasine.

3. Ammination of Anabasine

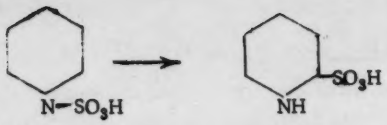
Soon after the structure of anabasine had been established, work was commenced on various derivatives of the latter and also on the study of the ammination reaction of anabasine and N-methyl-anabasine.

Orekhov and Norkin [24] and later Zhdanovich and Menshikov [25] synthesized a number of N-alkyl and N-aryl derivatives of anabasine. Menshikov, Grigorovich and Orekhov [26] and later Kabachnik and Katsnelson [27] made a detailed study of the ammination of anabasine and N-methyl anabasine in different solvents. In their work they showed that α and α_1 isomers are formed and they then proceeded to the synthesis of different compounds from the amminated products. Kabachnik and Zitser [28] in particular obtained acetylation products of N-methylamino-anabasines which are of definite interest pharmacologically. We have studied the ammination of anabasine and of N-methylanabasine under different conditions (without solvents, under pressure, without pressure and in the presence of different catalysts). As a result of this work we established the optimum conditions (temperature, proportions of reagents, effect of time and pressure) on the yield of reaction products, thus working out a comparatively simple method for the synthesis of amminated derivatives of anabasine and N-methylanabasine. We proceeded to prepare various derivatives of the latter (sulfanilamide derivatives, acetylation and methylation products).

4. Sulfonation of Anabasine.

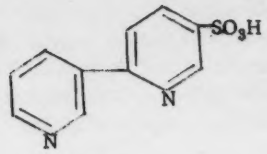
One section of the chemistry of anabasine which was studied was the sulfonation. The sulfonation of heterocyclic compounds has been the subject of many papers. Here we shall consider only the work of Terentyev and his school on the sulfonation of five-membered heterocyclic compounds [29]. It is known that these compounds are characterized by their high sensitivity to acids and therefore their sulfonation is often not possible with the usual sulfonating agents. For the sulfonation of similar compounds Terentyev successfully used pyridine sulfotrioxide, which had previously been used in the preparation of sulfamic acids (the sulfo group at the nitrogen). Terentyev and his co-workers obtained, in addition to the N-sulfamic acids, also various C-sulfonic acids of furan, thiophene, pyrrole, coumarone and indole.

We carried out the sulfonation of anabasine and its derivatives by means of pyridinesulfotrioxide in sulfuric acid. The preparation of N-sulfamic acid of anabasine from pyridinesulfotrioxide was carried out by the method of Rubtsov [30] who used this reagent for the sulfonation of piperidine. As the author himself notes, he did not succeed in separating the N-sulfamic acid. Instead of this the 2-sulfo acid of piperidine was formed. When we sulfonated anabasine under these conditions we obtained the N-sulfamic acid, which was separated and characterized as the potassium salt. Attempts to prepare the C-sulfonic acid from the N-derivatives of anabasine (N-methyl, N-acetyl) gave negative results. In order to compare the behavior of the anabasine piperidine nucleus with piperidine, N-methyl and N-acetyl piperidine were sulfonated. In this case also we did not succeed in obtaining 2-piperidine sulfonic acid. From this it was possible to draw the conclusion that the secondary nitrogen is of a different character. The nitrogen of the piperidine nucleus in anabasine is more basic than that in piperidine and the formation of 2-piperidine sulfonic acid is connected with the isomerization of the sulfo group from nitrogen to the α-carbon atom.



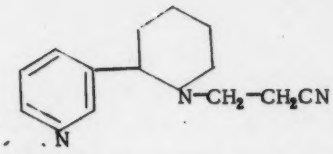
The sulfonation of anabasine by means of pyridine sulfotrioxide at 100-200° yielded no sulfonation products; at 200° isomerization of the pyridine sulfotrioxide to β pyridine sulfonic acid took place.

Sulfuric acid sulfonates anabasine at 300-320° with the formation of the monosulfonic acids of α-β-dipyridyl. The same acid was obtained when N-acetylanabasine was sulfonated. From an extensive study of the properties of the anabasine sulfonic acids and their conversion products, we were able to establish the structure of this compound.

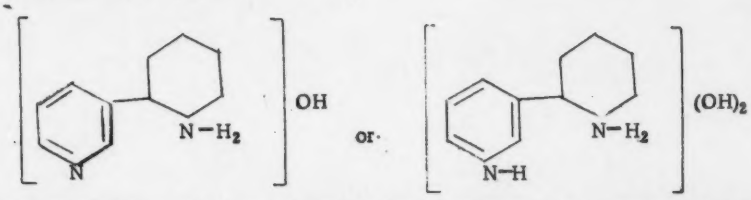


5. Cyanethylation of Anabasine

Over the past two or three decades many papers have appeared in the chemical literature dealing with the addition to acrylonitrile to the most diverse compounds, mainly organic, containing mobile hydrogen atoms. By means of this reaction, termed cyanethylation, β-substituted derivatives of propylnitrile and their conversion products became available. Many of the compounds obtained have an important practical value. We have studied the reaction between anabasine and acrylonitrile and ethylenecyanhydrin: N(β-propionitrile) anabasine has been prepared and characterized:



The effect of water on the rate of reaction between anabasine and acrylonitrile was studied. The cyanethylation reaction in aqueous solution has previously been described for ammonia and for a great number of aliphatic and alicyclic amines, but mainly in the presence of catalysts. Our experiments show that for anabasine the reaction with acrylonitrile without a catalyst proceeds at a moderate rate and only on heating. Water greatly increases the rate of this reaction. Anabasine is soluble in water with slight evolution of heat due to the partial formation of hydrates of the ammonium bases:



These ammonium bases, which are present in the reaction mixture, catalyze the addition reaction of anabasine to acrylonitrile by an ionic mechanism. This reaction mechanism which we have proposed has been confirmed by reactions in other solvents (e.g., petroleum ether). Quaternary ammonium bases (triton B, Rodionov's catalysts) have previously been proposed as additives to the cyanethylation reaction. When the reaction between acrylonitrile and anabasine in solvents was carried out in the presence of catalytic quantities of alkalies, quantitative yields of N(β-propionitrile) anabasine were obtained. This enabled us to work out a laboratory method for the separation of lupinine from mixtures with anabasine.

N(β-propionitrile) anabasine was used for further synthesis and conversions. When this was hydrolyzed with concentrated sulfuric acid N(β-propionamino) anabasine, N(β-aminoethyl) anabasine and N(β-carboxyethyl) anabasine were obtained. Hydrogenation of N(β-propionitrile) anabasine resulted in the separation of N(γ-aminopropyl)-anabasine and di[γ(N-anabasino)propyl]-amine. The following derivatives of N-(β-propionitrile) anabasine were obtained: N(γ-acetylamino)propyl)-anabasine, γ-N-anabasino propylethylurethane.

the ethyl ester of the γ-(N-anabasino)propylaminoacetic acid and N,N'-di[γ-(N-anabasino)-propyl]-urea.

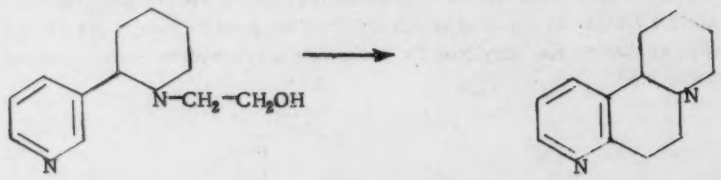
Thus, there are obtained ten new compounds as a result of the interaction of anabasine and acrylonitrile.

6. Reaction between Anabasine and Aliphatic Oxides

The work of many investigators, as well as our own, on the study of the alkaloids of plants, especially of A. aphylla at different vegetation stages has shown that the quantity of proportions of the different alkaloids in the plant is not constant. The question of the formation and the dynamics of accumulation of the alkaloids in the plant organism, as well as the part they play in the life process of the plant, has not been finally answered. It is also not entirely clear how alkaloids of one type of structure disappear during the course of the vegetation period with the formation of alkaloids of another structure with entirely different chemical structures.

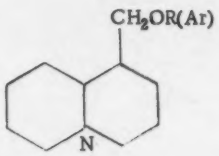
One method of studying the problem of alkaloid transition is to synthesize various intermediate compounds and to study the chemical conversion undergone by the alklaoids. This work, as well as being of great theoretical interest, has also practical value, since the intermediate products synthesized may possess physiological activity. Moreover, in studying changes in the structure of alkaloids it may be possible to find at what point new physiological properties make their appearance. For example, it is known that anabasine has insecticidal and other properties not possessed by other alkaloids. Thus, proceeding from anabasine to aphyllidine, or in the reverse direction, it may be possible to find when the new physiological properties appear.

One of the substances used for the preparation of these intermediate products in the study of A. aphylla alkaloids was the amino alcohol of anabasine which we had previously synthesized N(β-hydroxyethyl) anabasine. When this was dehydrated with phosphoric anhydride a crystalline base was obtained which possessed the systems of norlupinane and pyridine and which was termed 4,5-(α,β pyridylen)-norlupinane

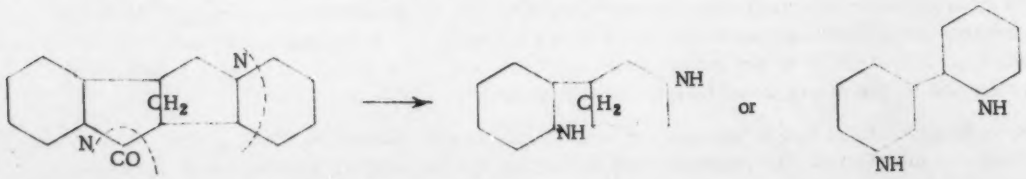


Work on the anabasine is also being carried out in other laboratories of our Republic. For example, we would mention the following: in the Institute of Chemistry of the Academy of Sciences Uzbek S.S.R. Talipov and co-workers [31] have studied the possibility of using anabasine in chemical analysis. Much work has been done on the study and synthesis of complex compounds of anabasine with salts of various metals by Udovenko, Azizov and co-workers [32]. In addition to anabasine we have also studied the secondary alkaloids of anabasine. Without going into details of the investigations of these alkaloids we may mention only a few results.

The methods which we worked out for the separation of anabasine-lupinine mixtures in particular with metallic sodium in hydrocarbons enables lupinine to be obtained in a satisfactory yield either as sodium lupinate or as the free base. Starting from sodium lupinate and chlorolupinane, we prepared a number of new compounds of the general formula [33]:



We have also studied the cleavage products of aphilline and aphillidine which are intermediate between the two structural types pachycarpine and α,β-dipiperidyl:



These investigations are directed toward finding several general methods for establishing the chemical nature of alkaloids of the C_{15} series (~30 of them are known). The importance of this work has greatly increased of late in connection with the use of aphilline as a substitute for novocaine.

The directives of the 19th Party Congress on the Five-year Plan for the Development of the USSR in 1951-55 stipulate a new increase in the development of science and technology.

"To improve the work of scientific research institutes and the scientific works of higher educational institutions, to fully utilize the scientific forces for the solution of important problems relating to the development of the national ecenomy for the dissemination of progressive knowledge and for the wide practical application of scientific discoveries;to cooperate with scientists in every possible way in the development of their theoretical problems in all branches of knowledge and to strengthen the connection between science and production." *

The mighty program for the development of the USSR outlined in the directives of the 19th Congress places great responsibility on the scientists of the Soviet Union. The work of the scientists of our Republic, and especially the chemists, must be directed toward the solution of the most important scientific problems connected with the development of industry, agriculture and especially cotton raising.

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Uzbekh SSR

Received 10 February 1953

* Directives of the 19th Party Congress on the 5th Five-year Plan for the Development of the USSR in 1951-55. Pravda Press, 1952, page 29.

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* See Consultants Bureau Translation, p. 131.

THE REACTIONS OF ACETYLENE WITH AROMATIC COMPOUNDS*

I. P. Tsukervanik

Acetylene has acquired great importance in modern synthetic chemistry. Thanks to the basic classical work of Kucherov, Favorsky, Zelinsky and many other Russian and Soviet chemists, various reactions of acetylene with inorganic and organic compounds are now widely used in industrial syntheses. In spite of the large amount of work on the chemistry of acetylene, several of its characteristics in known syntheses have not been studied up to now. In particular, the problem of the nature of the interaction of acetylene with aromatic compounds has not been solved; in other words, the problem of the alkylation of the aromatic nucleus by acetylene has not been elucidated. For comparison, it should be noted that in the case of ethylene and its homologs this alkylation has been well studied and is utilized on the industrial scale. We have selected this problem for treatment because it is closely connected with investigations of aromatic nuclear alkylation reactions on which we have been working for some time.

Acetylene, having a triple bond, may be considered as reacting in successive stages with rupture of the multiple bonds. In the first stage vinyl aromatic compounds should be obtained, and in the second, diarylethanes:

$$CH{\equiv}CH + ArH \rightarrow ArCH{=}CH_2 \qquad (1)$$

$$CH{\equiv}CH + 2ArH \rightarrow (Ar)_2CH{-}CH_3 \qquad (2)$$

Step-wise additions to acetylene are well known for many of its other reactions, and it would naturally be expected that the processes shown would be possible. Therefore, acetylene should be compared with bifunctional reagents (for example, with dihalogen derivatives, glycols, halogenhydrins, etc.), whose functional groups take part in alkylations either successively or simultaneously. The possibility of directing the reactions depends on the correct choice of conditions based on a study of the mutual influence of atoms and groups in the organic molecules entering into, and produced in, the synthesis.

In a number of previous papers [1, 2], we have shown that it is possible to direct the course of alkylation by bifunctional groups. The study of the condensation of benzene and anisole with vinyl ethers is closely related to the present problem [3]. In spite of the ease with which these ethers undergo polymerization and hydrolysis in the presence of aluminum chloride, conditions could be found under which the reaction took place at the double bond. α-Phenylethylbutyl ether was obtained from benzene:

$$CH_2{=}CH{-}OC_4H_9 + C_6H_5H \xrightarrow{AlCl_3} CH_3{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}OC_4H_9$$

We considered it necessary to dwell on these points in order to bring out the connection between the present problem and our other studies which cover much material of value in its solution. This introduction is also necessary because the unfounded and false view that it is impossible to add one molecule of benzene or a benzene derivative, to acetylene, has often been put forward in the literature. We have already given a detailed study of the relevant literature [4].

The possibility of effecting the practical alkylation of the benzene nucleus by acetylene is very good. Vinylbenzene is a most important raw material used in the manufacture of synthetic rubber and plastics. Several previous attempts in this direction gave negative results. Not only was vinylbenzene not obtained, but the diarylethanes were obtained in good yield only in isolated cases (ditolylethane). Either the condensation of acetylene with benzene did not proceed far, or else high-polymer insoluble resins, different from the ordinary polystyrenes, were obtained. Some authors, on the basis of their experimental work, consider that acetylene reacts at once only with two molecules of an aromatic compound [5]; others attempt to account for the formation

* Paper read at a combined session of the Division of Chemical Sciences, Acad. Sci. U.S.S.R., and the Academy of Sciences, Uzbek. S.S.R., 25, X. 1952, Tashkent.

of insoluble resins by suggesting a special intermediate vinyl compound ("protostyrene") [6]. It should be mentioned that in one of the older papers [7] it is reported that styrene was obtained as the main product of the condensation of benzene and acetylene. Later workers have not been able to confirm these results.

We commenced the study of the condensation of acetylene with benzene by showing the possibility of using different catalysts and the effect of different conditions on the course of the reaction. A large number of experiments were then carried out with toluene, naphthalene, anisole, chlorobenzene and dimethylaniline. The reactions were carried out not only with acetylene but also with vinyl chloride and with acetaldehyde. It was found that under the usual alkylation conditions, either insoluble resins (with active aluminum chloride at 60-80°), or small yields of diarylethanes (with moist aluminum chloride at 20°-40°) were obtained. In the reaction with benzene, in addition to 1,1-diphenylethane, the by-products ethylbenzene, 9,10-dimethylanthracene and a high-boiling resinous substance were produced. In this series of experiments our condensations with naphthalene, anisole and chorobenzene gave negative results [8].

In further benzene condensations, we used aluminum chloride containing various additives designed to reduce its activity. It was found that the addition of ferric chloride, and some other substances, increases the relative yield of low-boiling products (100-150°). Styrene was separated from these products and identified. In individual experiments the yield of styrene mounted to 15% of the total reaction product. In addition, distyrene was separated from the high-boiling fraction [9].

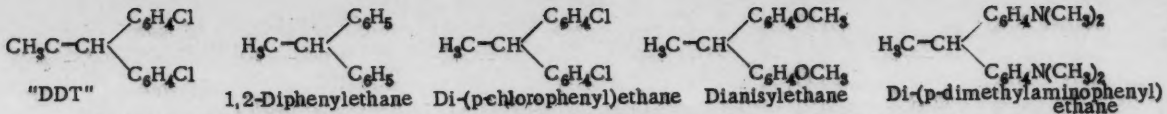
Thus, we showed that it was possible in principle to obtain aromatic vinyl compounds by the alkylation of acetylene. However, the total yield of products remained low. In order to raise the yield, it was necessary to carry out the condensation with active catalysts at high temperatures, at the same time avoiding the formation of insoluble resins. These resins are possibly polycondensation products of the diarylethanes. Korshak and his co-workers [10] have made a detailed study of the conditions and mechanism of formation of the aliphatic-aromatic polycondensation process. The condensation of benzene with dichloroethane with the formation of insoluble high-polymer resins similar in appearance to our resin is a reaction very closely related to our reactions. According to Korshak and his co-workes, an excess of dichloroethane is the main condition for the success of these polycondensations: with an excess of benzene, dibenzyl is formed. We established that 1,1-diphenylethane with an excess of dichloroethane also gives an insoluble resin. In studying afresh the condensation of dichloroethane with benzene, we found a number of supplementary conditions which promote high yields of dibenzyl.

Using these results we began to carry out the acetylene alkylations with the aromatic compounds in large excess and with reduced quantities of aluminum chloride at 40-60°. Under these conditions the insoluble resins were not formed at all, and the yields of the diarylethanes were greatly increased. 1,1-Diphenylethane was obtained in a yield of 55% of theory based on the acetylene consumed; chlorobenzene gave di-(p-chlorophenyl)-ethane in a yield exceeding 75% of theory; anisole gave dianisylethane in a yield of ~75%. In the latter case the possibility of using aluminum chloride activated with mercuric chloride was also shown [11]. The condensation of dimethylaniline with acetylene, acetaldehyde and vinyl chloride was studied in detail. Di-(p-dimethylamino-phenyl)-ethane was obtained in a yield of up to 50% of theory. In this synthesis the possibility of the occurrence of an anomalous oxidative condensation leading to amino-derivatives of diphenylmethane and triphenylmethane was noted [12].

These condensation products with chlorobenzene, anisole and dimethylaniline are compounds which have been little studied. They had been obtained in these condensations only in traces. Further work in this direction will doubtless lead to an increase in the number of acetylene-alkylated aromatic compounds; obviously, an increase in the yield of the diarylethanes may also be achieved.

Thus, as a result of a study of the condensation of acetylene with organic compounds, we succeeded, in spite of data to the contrary in the literature, in carrying out the two reactions given in the equations above. We can speak of a new simple method for the synthesis of diarylethanes. On the other hand, we have every reason to affirm the possibility of synthesizing the aromatic vinyl compounds. The acetylene alkylation reaction can be directed in the same way as other similar reactions.

As well as studying different variants of the condensation, we began a systematic study of the diarylethanes for the purpose of utilizing them in various syntheses. We carried out the main reactions in which nuclear and side-chain hydrogen atoms are replaced —chlorination, nitration and sulfonation. Chlorination of the diarylethanes might lead to substances similar to a group of insecticides. The diarylethanes have the same carbon skeleton as "DDT". Both the chlorination and the nitration of the diarylethanes should therefore give a series of new substances with possible insecticidal properties:



"DDT" 1,2-Diphenylethane Di-(p-chlorophenyl)ethane Dianisylethane Di-(p-dimethylaminophenyl) ethane

By chlorinating diphenylethane with heating and irradiation we obtained a high yield of the trichloroderivative, and on distillation this split off hydrogen chloride to give diphenyldichloroethylene. The composition and structure of the products have been shown by one of us [13].

$$(C_6H_5)_2CH{-}CH_3 \longrightarrow (C_6H_5)_2CClCH_3 \longrightarrow (C_6H_5)_2C{=}CCl_2.$$

On nitration, diphenylethane gave di-(p-nitrophenyl)-ethane [14] in 60% yield. On sulfonation, the p-disulfonic acid was obtained.

Finally, it is necessary to consider several general questions, connected with the working out of the problem. In the Directives of the XIX CPSU Congress the necessity of working out theoretical problems in all branches of knowledge is pointed out. In the field of organic chemistry, the basic theoretical problems were defined by the All-Union Conference on the Theory of Chemical Structure. In the Conference resolutions the following is placed among the problems regarded as of the first importance: "It is necessary that Soviet scientists should center their attention on deepening and extending our knowledge of the chemical structure of matter and on the development of the theory of the mutual influence of atoms in the molecule. It is necessary to work out problems on the dependence of molecular reactivity on structure and reaction medium."

It is just this problem which we have in mind in our work. Studies on the alkylation of aromatic compounds are still often limited by fixed views on the possibility of effecting and directing reactions. Meanwhile there is no doubt about the possibility of directing a synthesis in one direction or another on the basis of a knowledge of the characteristics of chemical structure and the effect of conditions. The study of a reaction direction which is difficult to bring about not only promotes the development of organic chemistry from the theoretical point of view, but also enables a number of practical tasks to be undertaken.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 54. ELEMENTARY REACTIONS OF THE POLYESTERIFICATION PROCESS

V. V. Korshak and S. V. Vinogradova

As a result of studies on the kinetics of the polycondensation process of hexamethylene glycol with sebacic acid, we showed that the mechanism of the process changes fundamentally in the different stages [1]. At first, when only the starting materials – hexamethylene glycol and sebacic acid – are present in the reaction mixture these interact. Water is thus eliminated and low-molecular-weight polyesters are formed giving a mixture which probably contains the following compounds:

$HO[CH_2]_6OOC(CH_2)_8COOH$ – acid ester of hexamethylene and sebacic acid,

$HO(CH_2)_6OOC(CH_2)_8COO(CH_2)_6OH$ – dihexamethyleneglycol ester of sebacic acid,

$HOOC(CH_2)_8COO(CH_2)_6OOC(CH_2)_8COOH$ – acid ester of hexamethyleneglycol and sebacic acid – hexamethylene-glycol disebacate, and

$H[O(CH_2)_6OOC(CH_2)_8CO]_2OH$ – the dimer.

After even half an hour the reaction mixture contained 60.9% of these low-molecular-weight polyesters, 33% of the starting-materials and only 6.1% of polyesters having a molecular weight higher than 900 (beginning with the trimer and higher). After 2.5 hours the amount of starting materials fell to ~ 4%, and the low-molecular-weight polyesters to 13.3%. However, the increase in molecular weight continued, from which it may be concluded, that the growth of the polyester molecule at this reaction stage is mainly due to the interaction of polyester molecules already formed.

Thus, the entire polyesterification process may be divided into two stages which differ sharply from one another in their reaction mechanisms: in the first stage the main reaction is between the starting materials, in the second the interaction of preformed polyester molecules predominates.

The low-molecular-weight monomeric starting materials react almost completely in the first stage of the process, and at the end of this the proportion of monomers present is so low that they play only a small part in the building up of polyester macromolecules.

However, their presence in small quantities is very necessary, because they play an essential part in catalyzing the process; in their absence the growth of polyester molecules is greatly retarded.

In the light of these results, it seemed of interest to study the separate elementary reactions of the polyesterification process, since it might be expected that their function and significance would differ in different stages. In the first stage of the polyesterification process, the main elementary reaction is obviously direct esterification, resulting from the interaction of alcohol and hydroxyl groups, and its mechanism may be established by studying the early stages of the polyesterification process, as has already been done by one of us in collaboration with Rafikov [2]. Therefore, in the present paper, we are concerned with finding if other possible reactions occur and with establishing their mechanisms.

We confined our studies to those intermediates which arise in the first reaction stage, and we investigated the diglycol ester of sebacic acid with the aim of finding out how it behaved under the polycondensation conditions and the possible routes of the conversions which it undergoes. The diethyleneglycol ester of sebacic acid was prepared by heating sebacic acid with an excess of ethylene glycol (recrystallized from benzene, melted at 60°). The diglycol ester thus obtained was heated under the conditions generally used in the polycondensation reaction at a temperature of 100 to 250°, under vacuum with a residual pressure of 1–2 mm. Tubes containing samples of the diglycol ester were heated for different times, varying from 1 to 30 hours and longer. Otherwise, the experimental

methods were those previously described [3]. The product samples were extracted from the tubes and their molecular weights determined by the viscosity method in 0.5% benzene solution. Two experiments were carried out at each temperature – one without a catalyst, and the other with 0.5% of hydrated lithium oxide. The results obtained are given in Table 1.

TABLE 1

Polycondensation of Sebacic Acid Diglycol Ester

Heating time, in hours	Molecular weight of polyesters obtained at temperature of					
	100°		150°		200°	
	without catalyst	with catalyst	without catalyst	with catalyst	without catalyst	with catalyst
1	–	–	197	–	520	1823
2	197	524	–	–	1100	2835
3	–	–	–	–	1288	4050
4	–	–	317	768	–	–
5	317	786	–	–	–	5377
6	–	–	550	–	2746	–
7	–	–	–	1047	–	–
8	942	1042	–	–	4644	7500
9	–	–	1012	–	–	–
10	–	–	1047	1047	4644	8520
11	942	1012	–	–	–	–
12	–	–	1047	–	5000	9393
14	–	–	1047	–	–	10022
15	–	–	–	1047	–	–
16	–	–	–	–	–	10757
17	–	–	1047	–	6076	–
18	–	–	–	–	–	11069
20	–	–	1047	–	7927	–
24	–	–	–	–	–	12360
28	–	–	–	–	8100	–

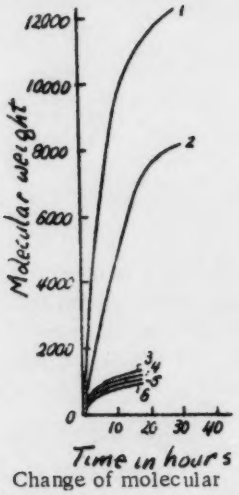

Fig. 1. Change of molecular weight with temperature: 1) Temperature 200° (cat.). 2) temperature 200° (without cat.); 3) temperature 150° (cat.); 4) temperature 100° (cat); 5) temperature 150° (without cat.); 6) temperature 100° (without cat.).

As will be seen from the results in Table 1, the molecular weight of the polyesters formed in the reaction increases with increasing temperature. This relationship is especially clear in Fig. 1 which is based on the results of Table 1.

It should be mentioned that at a temperature of 200°; side-reactions, in which the polyester was decomposed, occurred; for this reason, the molecular weight values obtained at this temperature are not trustworthy.

Thus, it may be concluded that when the diglycol ester is heated polycondensation proceeds through a transesterification mechanism in which the hydroxyl groups of one molecule react with the ester links of another, as shown by the following equations:

$$HOCH_2CH_2OOC(CH_2)_8CO\,|\,OCH_2CH_2OH$$

$$+$$

$$HOCH_2CH_2OOC(CH_2)_8COOCH_2CH_2OH \rightarrow HOCH_2CH_2OOC(CH_2)_8COOCH_2CH_2OOC(CH_2)_8-$$

$$-COOCH_2CH_2OH + HOCH_2CH_2OH$$

The total polycondensation reaction may be expressed in the following form:

$$x\,HOCH_2CH_2OOC(CH_2)_8COOCH_2CH_2OH \rightarrow (x-1)HOCH_2CH_2OH + H[OCH_2CH_2OOC(CH_2)_8CO-]_x OCH_2CH_2OH$$

As will be seen from these equations, the polycondensation proceeds with the simultaneous separation of glycol, which is removed from the reaction sphere, and this promotes the process in which the polyester molecules are enlarged. Therefore, this case is another in which we have an equilibrium exchange reaction, the position of equilibrium depending on the rate of removal of the low-molecular-weight reaction products, as in other examples of polycondensation [4].

We have previously studied the kinetics of the transesterification reaction of esters with alcohol [5]. Ethyl

stearate and cetyl alcohol were used and the studies were carried out at 122, 168, 183, and 250°, both with and without catalysts; the catalyst used was 1% of either sulfuric acid or sodium cetylate. It was found that the reaction rate and the extent of conversion increase with increasing temperature. The activation energy of the reaction at 170° was 12,950 cal/mole and the temperature coefficient, 1.34. This reaction was very sensitive to catalysts, the presence of which caused a marked increase in the rate. Thus, at a temperature of 183° without a catalyst the conversion reached 12.2%, while in the presence of sodium cetylate it amounted to 35%, and with sulfuric acid, to 61.5%. At lower temperatures, no reaction at all took place, but with increase in temperature the degree of conversion constantly increased. Thus, at 250°, the conversion was 36.3%, without a catalyst, and 66.6% with sodium cetylate. These results obtained with low-molecular-weight compounds such as ethyl stearate and cetyl alcohol [5] may be used in examining the polycondensation reaction of sebacic acid diglycol ester, since the mechanism of both processes is evidently the same. Moreover, a comparison of the results obtained in studies of both reactions shows their great similarity.

It was of interest to study the growth process of the macromolecular chains in this reaction, in order to compare it with the glycol and acid polycondensations which we have studied previously [1]. For this purpose, samples of sebacic acid diglycol ester were heated in tubes at a temperature of 200° and a residual pressure of 1-2 mm. After the heating, which was carried out for varios times, the content of free hydroxyl groups in the reaction product was determined; and the low-molecular-weight polyester fraction was separated from the high-molecular-weight fraction by extracting the product with a mixture of petrol ether and ethanol (4.5:5.5) for two hours with regular shaking. Control experiments showed that this solvent dissolves polyesters having molecular weights up to 900. The polyesters could thus be separated into two parts: a high-molecular-weight fraction of esters of molecular weight above 900, and a low-molecular-weight fraction of molecular weight less than 900. The results obtained are shown in Table 2.

TABLE 2

Heating time in hours	No. of ml of 0.02 N sodium hydroxide required in titration of hydroxyl groups in 1 g of polyester	% of		Molecular weight	
		High-molecular weight-polyester	Low-molecular weight polyester	Of high-molecular-weight polyester as shown by viscosity	Of low-molecular-weight polyester by end-group method.
0.0	334.8	0.0	100.0	—	—
0.7	213.0	2.1	97.9	997	847
2.0	97.5	24.9	75.1	1576	1449
3.0	92.5	55.9	44.1	1664	1538
6.0	41.9	91.8	8.1	2926	2857
9.0	23.8	98.2	1.8	4722	4545
12.0	21.7	98.3	1.7	5084	5000
17.0	18.0	98.3	1.7	6153	6060

The results of Table 2 show that the polycondensation of the diglycol ester proceeds in such a manner that at first a low-molecular-weight polyester is the main product, which is then converted to a high-molecular-weight form. This is made particularly clear in Fig. 2, which is based on the results in Table 2.

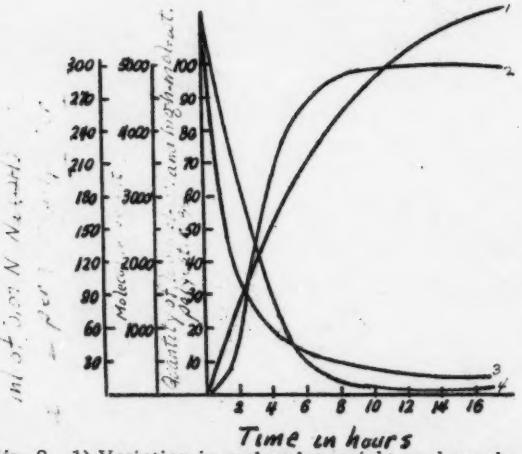

Fig. 2. 1) Variation in molecular weight as shown by viscosity. 2) variation in amount of high-molecular-weight polyester; 3) variation in amount of 0.02 N NaOH in cc. for titration of hydroxyl groups in 1 g of polyester. 4) variation in amount of low-molecular-weight polyester.

From a comparison of curve 4, showing the variation of low-molecular-weight polyester content of the reaction mixture, with curve 3, showing the variation in the hydroxyl group content, it may be seen that a rapid reduction in the content of hydroxyl groups is followed by a sharper fall in the proportion of low-molecular-weight-polyester. This is evidently explained by the initial separation of a large quantity of ethyleneglycol, but in the later stages of the reaction, when longer chains are reacting, this process takes place to a considerably lesser extent. The curve for the proportion of high-molecular-weight polyester, 2, rises rapidly in the first six hours, and changes only slowly, while the curve for molecular weight increases, 1, continues to rise. From this it may be concluded that the further increase in molecular size is due, not to the monomer of which little remains, or to

the low-molecular-weight polyester, is to the interaction of high-molecular-weight polyester molecules.

The picture observed in the case of the diglycol ester polycondensation is thus very similar to that which is observed in the polycondensation of glycol with a dicarboxylic acid, which we have already described [1]. This great similarity in the course of the formation of polyesters from these different starting materials suggests that it is the result of deep-seated causes. Evidently, it may be supposed that in the polycondensation reaction of glycols with dicarboxylic acids the increase in molecular size in the second stage of the process proceeds by way of a trans-esterification reaction, similar to that which occurs in the polycondensation of the diglycol ester, and not directly by the interaction of terminal hydroxyl and carboxyl groups, the concentration of which has become very low at this stage.

SUMMARY

1. The elementary reactions of the polyesterification process have been examined and it has been shown that the increase in molecular size at different reaction stages is due to different mechanisms.

2. The polycondensation of sebacic acid diglycol ester has been studied.

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MACROMOLECULAR COMPOUNDS. COMMUNICATION 57.

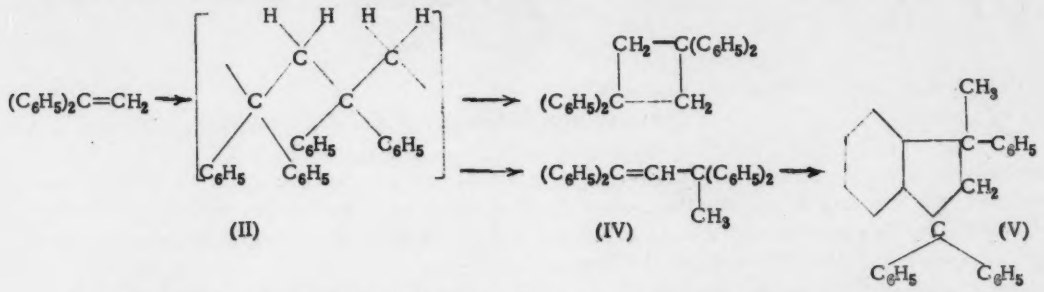
THE RELATION BETWEEN THE POLYMERIZATION CAPACITY AND THE STRUCTURE OF SOME UNSYMMETRICAL DIARYLETHYLENES

V. V. Korshak and N. G. Matveeva

In a previous paper we examined the question of the effect of stereochemical factors on the polymerization capacity of halogen-substituted ethylenes [1]. As a result of this investigation it was shown that steric hindrance to polymerization arises when the substituted ethylene molecule contains a large number of substituents of considerable size [2].

It was found that in the case of the halogen-substituted ethylenes, steric hindrance occurs only when three or four substituents are present, or with two when these are symetrically disposed. If the two halogen atoms are unsymmetrically disposed in relation to the double bond, then their screening effect is not great enough to interfere with polymerization, and for this reason all compounds of this type, such as vinylidene fluoride, chloride, bromide and iodide, polymerize very easily [1].

Still earlier, one of us in collaboration with Samplavskaya, suggested an explanation for the fact, which was observed by Lebedev [3], Belov [4] and other workers, [5], that unsymmetrical diphenylethylene, which also has only two substituents, forms only the dimer and gives no polymer [5]. In this case the cause of the early termination of the polymerization reaction may be seen in the development of strong steric strains in the molecule of the intermediate which is formed by the union of two monomer molecules. The reaction scheme previously put forward for the dimerization of 1,1-diphenylethylene is given below [5]:



(II) (IV) (V)

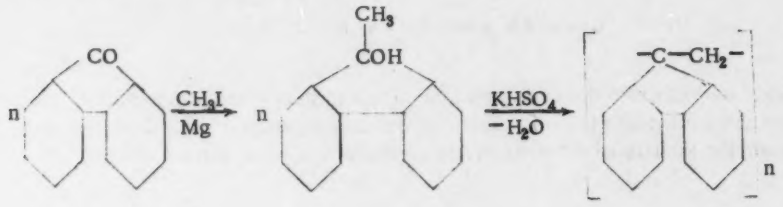
Thus, the first reaction stage consists of the formation of a biradical dimer (II). Like all free radicals which are intermediates in radical polymerization reactions, this intermediate is extremely reactive and unstable. Unusually, in the case of other polymerized compounds the reacton goes further, a third, fourth, etc., molecule adding to the type (II) product to give finally a long high-polymer chain. Because of stereochemical factors, such a process does not occur in this case. The large volume of the phenyl groups at the 1 and 3 carbon atoms, precludes the possibility of the usual zig-zag arrangement of carbon atoms, as shown in the scheme for product (II), and forces them into an arrangement in which either the molecule is planar forming a butane ring or the valence angles become deflected and the molecule is isomerized to the stable structure 1,1,3,3-tetraphenyl-butene-1(IV), which easily isomerizes to 1,1,3-triphenyl-3-methylhydrindene (V). It is easy to see that the cause of these strong steric stresses must be the phenyl groups, if the large volume which these occupy is considered; this is clear from Fig. 1 which represents a stereochemical model of 1,1-diphenylethylene.

That the dimerization of unsymmetrical diphenylethylene is due to effects of a stereochemical kind, and not to other causes, is clear from a comparison of the properties of this compound with those of isobutylene, the polymerization of which was studied by Butlerov as long ago as 1873 [6]. It is well-known that in the presence of ionic catalysts at low temperatures, isobutylene gives a very high-molecular-weight polymer [7]. An increase in the volume of even one of the substituents makes a fundamental change in the polymerization capacity. Thus, α-methylstyrene, because of the large volume of one of the substituents, fails to undergo radical polymerization when subjected to the action of heat, light or peroxides; but it is capable of forming a polymer under the influence of ionic catalysts, which are more active and better able to overcome steric hindrance than are the initiators of radical

polymerization, as we have already shown [8]. In this connection, it seemed of interest to examine the problem of how changes in the position or structure of substituents affected the polymerization capacity of diphenylethylene.

There are references in the literature which indicate that diphenylethylene polymerizes on heating [9]. However, the polymerization conditions and the properties of the polymer have not been described in detail, and therefore, a study of this compound seemed of definite interest.

We prepared diphenylethylene by dehydrating 9-methylfluorenol, which was obtained from fluorenone and methylmagnesium iodide by the following reactions:



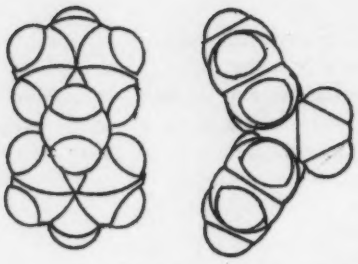


Fig. 1. Stereochemical model of the 1,1-diphenylethylene molecule

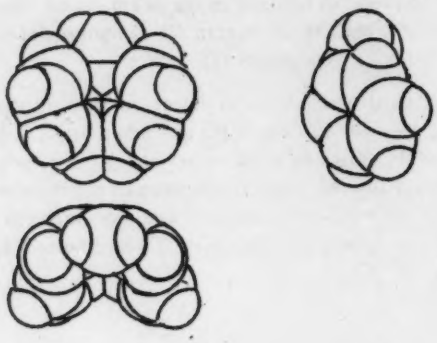


Fig. 2. Stereochemical model of the diphenylenethylene molecule.

Diphenylenethylene, formed by the dehydration of 9-methylfuorenone, polymerizes at once, and in none of our experiments were we able to separate the monomer. After reprecipitation, the diphenylenethylene polymer was obtained as a white powder, very soluble in benzene and in toluene but insoluble in alcohol, ether and water. The polyphenylenethylene softened at a temperature of 155-165°.

Thus, in spite of their great structural similarity, diphenylenethylene and 1,1-diphenylethylene differ in their tendency to polymerize; this is difficult to understand at first glance. If we examine the stereochemical model of diphenylenethylene shown in Fig. 2, and compare it with the molecule of 1,1-diphenylethylene in Fig. 1, the vast difference in the structure of these compounds becomes apparent at once.

In 1,1-diphenylethylene both the phenyl groups are entirely free and can easily rotate, and for this reason the space they occupy is greatly increased; but in diphenylenethylene, because of the presence of a bond between the phenyl groups, these are very compactly arranged and are not capable of free rotation round the ethylene carbon-carbon bond; they therefore do not cause steric hindrance to the same extent as we find in 1,1-diphenylethylene.

It should be added that in 1,1-diphenylethylene the phenyl groups have a strong screening effect on the ethylene carbon atoms which play an active part in the polymerization; these are prevented from touching, but the steric strains produced in the dimer molecule as a result of the mutual repulsion of the phenyl groups lead to isomerization of the biradical finally causing rupture of the chains of the growing molecule at the dimer stage, as shown in the reaction scheme (p. 487).

On the other hand, the phenyl groups in diphenylenethylene are so placed that the carbon atoms between which new bonds are formed in polymerization are easily accessible, and there is nothing to hinder the increase

in chain length with the formation of a high-molecular-weight product. Here there is evidently no marked screening effect which might hinder the diphenylenethylene polymerization.

EXPERIMENTAL

Fluorenone

Forty grams of fluorene and 80 ml of acetic acid were placed in a flask fitted with a reflux condenser and a dropping-funnel and heated to gentle boiling [10]. A solution containing 135 g of potassium dichromate in a hot mixture of 160 ml of acetic acid and 40 ml of water was slowly added. During the dichromate addition the heating was stopped, since the heat of reaction caused the mixture to boil. When all the dichromate had been added boiling was continued for a further 3 hours. The reaction mixture was then poured into ice-water and set aside for 3 hours, after which it was filtered through cloth; the residue was washed, at first with dilute sulfuric acid and then several times with water, and dried in air.

The air-dried fluorenone was placed in a Claisen flask and distilled into a Würtz flask until a bright orange oil appeared. To remove fluorene, the fluorenone was dissolved in benzene (about 1 ml per gram) and the solution poured into twice its volume of petroleum ether. The fluorenone which was precipitated in large crystals was collected at the pump. The yield was 33.7 g or 73% of theory. The fluorenone melted at 83-84°.

9-Methylfluorenol

Methylmagnesium iodide was prepared from 2.4 g magnesium, and 14.2 g of methyl iodide in 50 ml of absolute ether [11] in a flask fitted with a reflux condenser and a dropping funnel. A solution of 18 g of fluorenone in 50 ml of ether was added with cooling to the methylmagnesium iodide. After all the fluorenone solution had been added, a few lumps of ice were placed in the flask and the reaction mixture was poured into dilute sulfuric acid. The ethereal layer was removed, washed several times with water and dried over sodium sulfate; the ether was then distilled off. The residue was recrystallized from benzene. Yield 10.3 g, i.e. 52.5% of theory.

9-Methylfluorenol consisted of white crystals melting at 176-177°.

Polydiphenylenethylene

9-Methylfluorenol (9.8 g) was placed in a flask and heated to 160-170° after 1 g of ignited potassium bisulfate and a little hydroquinone had been added. The solid polymer formed, was dissolved in benzene, washed with water, dried over sodium sulfate and precipitated by pouring the solution into excess of methanol. Polydiphenylethylene consisted of a white powder, melting at 155-165°; very soluble in benzene and in toluene and insoluble in alcohol, ether and water. Yield 53.03% of theory. Molecular weight by viscosity in benzene solution, 4890.

	Found %:	C 93.80; 93.50; H 6.07; 6.08
$C_{14}H_{10}$	Calculated %:	C 94.34; H 5.65

SUMMARY

1. The absence of steric hindrance to polymerization in diphenylenethylene is explained on the basis of the compact arrangement of the phenyl groups in the molecule.

2. Stereochemical models of diphenylethylene and 1,1-diphenylethylene are examined and an explanation is given for the different behavior of these compounds in the polymerization reaction.

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MACROMOLECULAR COMPOUNDS.

COMMUNICATION 58. STERIC HINDRANCE IN THE POLYMERIZATION OF NUCLEAR-SUBSTITUTED STYRENES

V. V. Korshak and N. G. Matveeva

In a previous paper we considered the question of the influence of stereochemical factors on the capacity for polymerization of a number of unsymmetrical disubstituted ethylenes and we found the reasons why diphenylethylene gives only a dimer while diphenylenethylene polymerizes very easily [1]. The study of steric hindrance produced by substitution in the styrene nucleus was also of interest and is considered in the present paper.

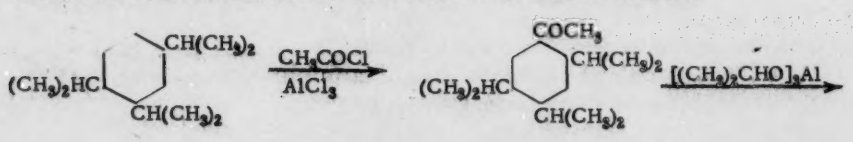
The first systematic study of the polymerization capacities of substituted styrenes was carried out by Shorygin and Shorygina [2]. They studied the polymerization of o-, m- and p-methylstyrenes, o- and p-aminostyrenes, o- and p-methoxystyrenes, o- and p-bromostyrenes, as well as other styrenes, and they established that these styrenes easily polymerize when they are heated to 170-175° for three hours or to 100° for 150 hours.

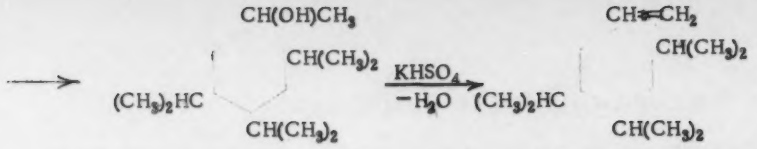
Later, a large number of nuclear-substituted styrenes were obtained and it was shown that the introduction of substituents of a given size into the meta or para position does not bring about hindrance to polymerization. Thus, the polymerization was described of meta- and para-butyl styrenes [3] and m- and p-cyclohexyl styrenes [3] chlorostyrenes [4] p-cyanostyrenes [5] m- and p-iodostyrenes [6], p-carboxystyrenes [7] as well as others [8]. The presence of one substituent in the ortho position does not bring about hindrance to the polymerization process, even when one or two other substituents are present in m- or p-positions of the styrene nucleus. Thus, various di- and tri-substituted styrenes were capable of undergoing polymerization; these had substitutents in the 2,3-, the 2,4-, the 2,5-, the 3,4, the 3,5, the 2,4,5- and the 3,4,5-positions. All the dichloro-substituted styrenes easily polymerized when they were irradiated with ultra violet light [9]. 2,3-, 2,4-, 2,5- and 3,4 dimethylstyrenes also polymerized under the influence of ultra violet radiation [10]. 4-chloro-3-fluoromethylstyrene, 4-chloro-2-trifluoromethylstyrenes, 2,5-, 3,5- and 3,4-di(trifluoromethyl)styrenes, 4-chloro-2,5-di(trifluoromethyl)styrene and 4-chloro-3,5-di(trifluoromethyl) styrene easily polymerized in the presence of perioxide [11] and 5-isopropyl-4-methoxy-2-methyl styrene polymerized under the influence of ultraviolet light [12].

Steric hindrance to polymerization arises only with two substituents in the ortho position, as we observed in 2,6-dimethyl-4-tertiarybutylstyrene, which almost completely lost its capacity for radical polymerization, while, however, retaining its capacity for ionic polymerization [13]. 2,4,6-trimethylstyrene also gives a low-molecular-weight polymer when it is heated for several days at a temperature of 200° [14]. In the case of ortho substituents of large size, as for example, 2,4,6-tri(trifluoromethyl)styrene [15] and 2,4,6-trinitrostyrene [16], the styrenes are completely incapable of undergoing polymerization. Although in the latter case the cause of failure to polymerize is not clear, it is possible that it is not entirely due to steric hindrance, since m-nitrostyrene also failed to polymerize [17], evidently because of the inhibiting action characteristic of nitro compounds. Finally, it should be mentioned that 2,6-dichlorostyrene polymerizes easily on irradiation with ultraviolet light [18].

Thus, the literature indicates that substituents in the m- and p-position do not produce steric hindrance, while the presence of two substituents in the ortho position in some cases hinders the polymerization of di-substituted styrenes. One substituent in the ortho position does not as a rule interfere with polymerization.

Our aim was to find the reason for, and study the nature of the action of ortho substituents in the styrene molecule and for this purpose we synthesized 2,4,5-triisopropylstyrene and 2,6-dimethoxystyrene. 2,4,5-triisopropylstyrene was obtained from 1,2,4-triisopropylbenzene which was converted to 2,4,5-triisopropylacetophenone by the action of acetyl chloride in the presence of aluminum chloride. The 2,4,5-triisopropylacetophenone obtained in this way was reduced with aluminum isopropoxide to 2,4,5-triisopropylphenylmethylcarbinol and this was converted to 2,4,5-triisopropylstyrene by heating with potassium bisulfate:





2,4,5-triisopropylstyrene was found to be a substance very liable to polymerize and was easily converted to a polymer by heating for four hours to 100°, or even on standing at room temperature for two months. After reprecipitation the polymer was obtained in the form of a white powder which softened at 180-195°; the polymer obtained at 100° had a molecular weight of 10,800 and the one obtained at room temperature, a molecular weight of 22,700.*

Thus, it may be concluded that the presence of such a large substituent in the styrene nucleus as the isopropyl group does not hinder polymerization. In Fig. 1, a stereochemical model of 2,4,5-triisopropylstyrene is shown.

From this figure it is evident that the free rotation of the vinyl group is somewhat limited by the presence of the isopropyl group in the ortho position, but all the same the vinyl group is completely accessible for contact with the vinyl group of another monomer molecule which is necessary for successful polymerization.

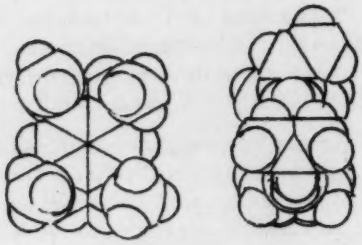
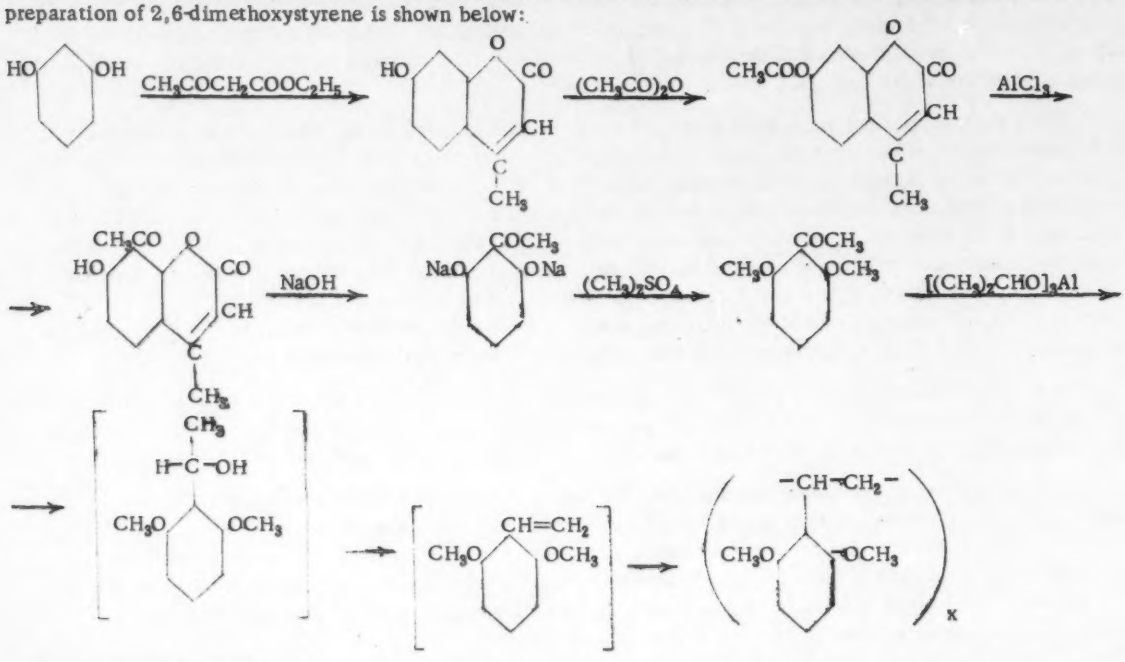


Fig. 1. Stereochemical model of 1,4,5-triisopropylstyrene.

2,6-dimethoxystyrene was obtained as a result of a long series of conversions from 7-hydroxy-4-methylcoumarin. The latter was obtained from resorcinol and acetoacetic ester in the presence of concentrated sulfuric acid. Acetylation of 7-hydroxy-4-methylcoumarin to 7-acetoxy-4-methylcoumarin, (Fries rearrangement of the acetoxy derivatives) and hydrolysis of the rearrangement product afforded 2-acetylresorcinol. Methylation of 2-acetylresorcinol by dimethylsulfate, reduction of 2-methoxyacetophenone by aluminum isopropoxide and dehydration of the carbinol formed resulted in the formation of 2,6-dimethoxystyrene which polymerized at once. The reaction scheme for the preparation of 2,6-dimethoxystyrene is shown below:



* The structure of 2,4,5-triisopropylstyrene which we synthesized was not confirmed experimentally, but it appears to be the most probable structure because the cases described in the literature of the introduction of the acetyl group into 1,2,4-trialkylbenzenes gave 2,4,5-trialkylacetophenones [25].

Poly-2,6-dimethoxystyrene consisted of a thick glasslike resin softening at 78-82° with a molecular weight of 3,000. In no experiment did we succeed in obtaining 2,6-dimethoxystyrene in the monomeric form, although we several times reduced with metallic sodium in ethanol and we attempted to follow exactly the conditions of this styrene synthesis described by Shamshurin [19]. This at-first-sight-unexpected tendency of 2,6-dimethoxystyrene to polymerize notably distinguishes it from 2,6-dimethyl-4-tertiarybutylstyrene, which we investigated previously, although the size of the methoxy group should be larger than the methyl, and it would be expected that 2,6-dimethoxystyrene would also lose its ability to undergo radical polymerization. The cause of this difference can only be found by examining the stereochemical models of the molecules of 2,6-dimethoxystyrene and 2,6-dimethyl-4-tertiarybutylstyrene which are shown in figures 2 and 3.

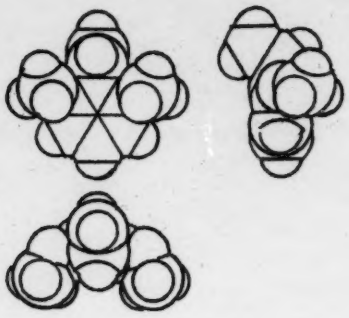


Fig. 2. Stereochemical model of the 2,6-dimethoxystyrene molecule.

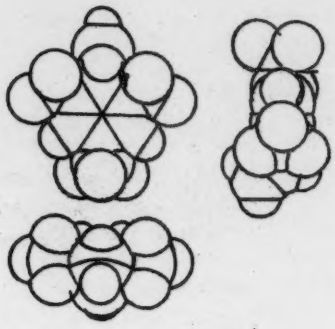
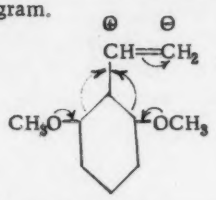


Fig. 3. Stereochemical model of the 2,6-dimethyl-4-tertiarybutylstyrene molecule.

As will be seen from these figures there is a great difference between these compounds. In the case of 2,6-dimethoxystyrene, the methoxy groups in the ortho position are capable of rotating and are so disposed as to allow completely unhindered rotation of the vinyl groups and do not screen them. That is, they do not bring about steric hindrance to polymerization. The oxygen atom, too, which is placed close to the vinyl group, is only slightly larger than the hydrogen atom (radius of the first is equal to 1.4 and of the second 1.2 A) and smaller than the chlorine atom (radius 1.7 A) and still smaller than the methyl group (radius greater than 1.7 A). Therefore, the atom of oxygen itself also does not hinder rotation of the vinyl group and brings about neither a screening nor a blocking effect. On the other hand, the presence of a methoxyl group as has been previously observed by one of us in collaboration with Kolesnikov et al [20] in 2-methoxy-1-vinylnaphthalene leads to the polymerization of the vinyl group and two oxygen atoms must still strongly polarize the double bond of the vinyl group and in this way increase its activity, as is shown in the following diagram.



On examining the arrangement of the 2,6-dimethyl-4-tertiary-butylstyrene we see a different picture. Two methyl groups in the ortho position hold the vinyl group as if in a pincers and do not allow it to come in contact with carbon atoms of another molecule, which is necessary if the polymerization process is to take place. We propose to call this effect "the blocking effect" to distinguish it from the screening effect caused by substituents attached directly to the carbon atoms of the vinyl group [21]. Naturally, the influence of the vinyl effect is greater the greater the size of the ortho substituents. For this reason it is easily seen why 2,6-dichlorostyrene can polymerize and why 2,4,6-tri(trifluoromethyl)styrene cannot, since the size of the trifluoromethyl group is much larger than the chlorine atoms of the methyl group, as can easily be seen in Figs. 3, 4, and 5.

EXPERIMENTAL

2,4,5-Triisopropylacetophenone

To a mixture of 30 g of 1,2,4-triisopropylbenzene, 15 g acetyl chloride and 100 ml tetrachloroethane,

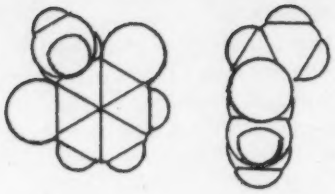


Fig. 4. Stereochemical model of the 2,6-dichlorostyrene molecule

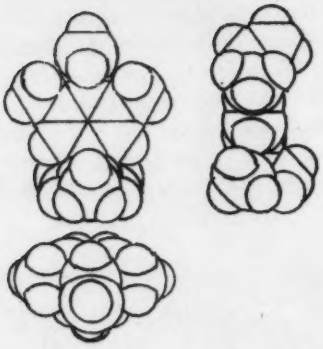


Fig. 5. Stereochemical model of the 2,4,6-tri(fluoromethyl)styrene molecule.

there was added, with cooling, 25 g of aluminum chloride in small portions. The mixture was allowed to stand overnight and then it was heated on a water-bath for an hour, after which it was decomposed by pouring into dilute hydrochloric acid. The organic layer was separated in a separator, washed several times with water and dried over sodium sulfate The tetrachloroethane was distilled off and the residue distilled under reduced pressure. The fraction boiling between 156-162° at 25 mm was collected and recrystallized from ethanol. Yield 22.5 g, i.e. 62.1% of theory. 2,4,5-triisopropylacetophenone consists of long white needles with a sharp incense-like smell, melting at 106-107°.

Found %: C 82.78; 82.60; H 10.76; 10.63
$C_{17}H_{26}O$. Calculated %: C 82.86 H 10.64

2,4,5-Triisopropylphenylmethylcarbinol

In a half-liter round-bottomed flask equipped with a reflux condenser were placed 200 ml of absolute isopropanol, 2.5 g of amalgamated aluminum and 0.5 g of mercuric chloride. The flask was then heated to boiling on a water-bath and 2 ml of carbon tetrachloride was added Almost at once a vigorous reaction commenced and the flask was cooled by means of cold water until the reaction subsided. After this the reaction proceeded to conclusion almost without heating, only at the end was heating on the boiling water bath required to dissolve the aluminum completely.

To the hot solution of aluminum isopropoxide in isopropanol, 10 g of 2,4,5-triisopropylacetophenone was addedand the mixture boiled for three hours. The reflux condenser was then changed for a straight condenser, the isopropanol and acetone distilled off, the residual mass was poured into water acidified with hydrochloric acid and 50 ml of benzene was added. The benzene solution was separated, washed with water and dried over sodium sulfate. The benzene was then distilled off. 2,4,5-triisopropylphenylmethylcarbinol was distilled under reduced pressure and the fraction coming over between 126 and 127° at 3 mm was collected. The yield was 58.03% of the theoretical. 2,4,5-triisopropylphenylmethylcarbinol after recrystallization from ether was obtained in the form of white needles melting at 93-94°.

Found %: C 81.90; 81.69; H 11.30; 11.38
$C_{17}H_{18}O$. Calculated %: C 82.29; H 11.36

Phenylurethane of 2,4,5-triisopropylphenylmethylcarbinol

To 2 g of 2,4,5-triisopropylphenylmethylcarbinol dissolved in 20 ml of absolute benzene, 1 g of phenylisocyanate was added and the mixture was boiled half an hour. The benzene was then distilled off and the phenylurethane recrystallized from alcohol. Yield 2.47 g or 82.6% of theory. Phenylurethane of 2,4,5-triisopropylphenylmethylcarbinol consisted of small white needles melting at 180-180.5°.

Found %: C 78.17; 78.35; H 9.10; 8.92; N 3.96; 3.87
$C_{24}H_{33}O_2N$. Calculated %: C 78.47; H 8.99 N 3.81

2,4,5-Triisopropylstyrene

In a Claisen flask 13 g of 2,4,5-triisopropylphenylmethylcarbinol and 2 g of potassium bisulfate were placed and the mixture distilled under reduced pressure so that styrene was distilled off at a temperature of 160-200°. The styrene collected was dried over sodium sulfate and redistilled once again under reduced pressure.

2,4,5-triisopropylstyrene boils at 165-166° at 75 mm. Yield 7.6 g, i.e. 63.12% of theory. d_4^{20} 0.9018; n_D^{26} 1.5075, MR_D 75.09. Calculated MR_D 76.89.

Found %: C 88.28; 88.41; H 11.18; 11.31
$C_{17}H_{26}$ Calculated %: C 88.62; H 11.36.

Polymerization of 2,4,5-triisopropylstyrene

1 g of 2,4,5-triisopropylstyrene was placed in an ampoule and the air was removed by repeated flushing with nitrogen. The sealed ampoule was placed in a boiling water bath and heated for four hours. The ampoule was then opened and the polymer reprecipitated by pouring a benzene solution into methanol followed by drying. The molecular weight by the viscosity method was found to be 10,800. Another sample of the styrene was allowed to stand at room temperature for two months. The molecular weight of this polymer was 22,700.

Found %: C 88.16; 88.50; H 11.12; 11.28
$C_{17}H_{26}$ Calculated %: C 88.62; H 11.36

7-Hydroxy-4-methylcoumarin

To 450 g of sulfuric acid (sp.gr. 1.84) cooled by a freezing mixture, there was added with stirring a mixture of 110 g of resorcinol and 130 g of aceto-acetic ester, at such a rate that the temperature of the reaction mixture did not exceed 0°. After the addition had been completed the mixture was allowed to stand at 0° for four hours with occasional stirring and it was then poured dropwise with vigorous stirring on to a mixture of ice and water. The bright yellow precipitate formed was removed by filtration and thoroughly washed with water and dried in air. The air-dried product was dissolved in dilute alkali and precipitated with hydrochloric acid [22]. Yield 162.3 g, that is 92.21% of theory. 7-hydroxy-4-methylcoumarin after recrystallization from ethanol consisted of a bright yellow powder melting at 188-188.5°.

Found %: C 68.07; 67.86; H 4.31; 4.48
$C_{10}H_8O_3$ Calculated %: C 68.17; H 4.57

7-Acetoxy-4-methylcoumarin

To a mixture of 30 g of alkali 100 ml of water and 500 g of ice, 88 g of 7-hydroxy-4-methylcoumarin was added. To the coumarin solution, still containing a certain amount of ice 60 g of acetic anhydride was added. The flask was closed with a stopper and vigorously shaken. The acetate, precipitated as a white mass, was filtered off, washed several times with water and dried in air [22]. Yield 96.3 g or 95.73% of theory. 7-acetoxy-4-methylcoumarin after recrystallization from ethanol was obtained as long, fine needles melting at 153-154°.

Found %: C 65.76; 65.42; H 5.02; 4.77
$C_{12}H_{10}O_3$ Calculated %: C 66.04 H 4.62

7-Hydroxy-8-acetyl-4-methylcoumarin

A mixture of 50 g of 7-acetoxy-4-methylcoumarin and 125 g of aluminum chloride was placed in a round-bottomed flask fitted with an air condenser and this was heated on a glycerol bath to 160° for three hours [24]. The reaction mixture was then decomposed by pouring it into ice-cooled dilute hydrochloric acid. The bright grey product formed was filtered off and washed several times with water. The product was then dissolved in a small quantity of 10% sodium carbonate solution. The insoluble part was removed by filtration and 7-hydroxy-8-acetyl-4-methylcoumarin was precipitated from the filtrate by the addition of hydrochloric acid. The precipitate was filtered off, washed with water and dried. Yield 11.2 g or 37.3% of theory. 7-hydroxy-8-acetyl-4-methylcoumarin after recrystallization from aqueous ethanol was obtained as small leaves of sandlike color melting at 167-168°.

Found %: C 65.47; 65.70; H 4.66; 4.73
$C_{10}H_8O_3$ Calculated %: C 66.04 H 4.62

Acetyl Resorcinol

In a 2-necked flask equipped with a reflux condenser, 26 g of 7-hydroxy-4-methylcoumarin and 240 mls of 12% solution of sodium hydroxide were placed and nitrogen was passed in through a tube not reaching quite to the surface; the flask was then heated on a boiling water bath for 6 hours [19]. The reaction mixture was then cooled and the acetyl resorcinol precipitated with hydrochloric acid and recrystallized from water. Yield 12.4 g

or 68.1% of theory. Acetyl resorcinol on recrystallizing twice from water was obtained as a bright yellow powder melting at 155-156°.

Found %: C 62.74; 62.82; H 5.39; 5.18
$C_8H_8O_3$. Calculated %: C 63.14; H 5.30

2,6-Dimethoxyacetophenone

In a 2-necked flask fitted with a reflux condenser and a dropping funnel, 12 g of acetyl resorcinol and 120 ml of 12% solution of sodium hydroxide were placed [19]. The reaction mixture was heated to boiling, the heating was then stopped and 100 g of dimethyl sulfate was added in small portions. When about 2/3rds of the dimethyl sulfate had been added, 60 ml of 12% solution of sodium hydroxide was added followed by the remainder of the dimethyl sulfate. Care was taken to keep the medium alkaline. The reaction mixture was then boiled for half an hour and after cooling the 2,6-dimethoxy acetophenone formed was filtered off, washed with water and recrystallized from water. Yield 10.2 g or 70.8% of theory. 2,6-dimethoxyacetophenone was a bright yellow substance melting at 69-70°. Shamshurin [19] gives a melting point of 72-73°.

Found %: C 66.34; 66.46; H 6.63; 6.84
$C_{10}H_{12}O_3$. Calculated %: C 66.66; H 6.71

2,6-Dimethoxystyrene polymer

Aluminum isopropoxide was prepared from 2.5 g of amalgamated aluminum and 100 ml of absolute isopropanol in a round-bottomed flask fitted with a reflux condenser as previously described. To the aluminum isopropoxide obtained, 10 g of dimethoxyacetophenone was added and the reaction mixture was boiled for 2½ hours, after which the reflux condenser was changed and the isopropanol and acetone were distilled off. When the isopropanol had been removed the residual mass was poured into water acidified with hydrochloric acid.

The aqueous layer was extracted with benzene. The benzene layer was washed several times with water and then dried over anhydrous sodium sulfate. The benzene was removed by distillation and a solid residue of polymer having a dark brown color and melting at 78-82° was obtained. Yield 5.8 g or 63.3% of theory. The molecular weight of poly-2,6-dimethoxystyrene determined by the viscosity method in benzene solution was found to be 3060. Attempts to prepare the monomer by depolymerization of the polymer were not successful since the monomer formed immediately polymerized on the walls of the flask as a solid layer.

Found %: C 72.88; 72.74; H 7.39; 7.36.
$C_{10}H_{12}O_2$. Calculated %: C 73.13; H 7.37.

The reduction of 2,6-dimethoxyacetophenone was also carried out with metallic sodium in ethanol by the method described by Shamshurin [19] but in this case also no monomeric 2-methoxystyrene was obtained.

SUMMARY

1. It is shown that the isopropyl group in the ortho position of the styrene molecule does not cause steric hindrance in the polymerization process.

2. It is shown that 2-methoxyl groups in the ortho position of the styrene molecule do not hinder polymerization.

3. 2,4,5-triisopropylacetophenone and 2,4,5-triisopropylstyrene have been synthesized.

4. Polymers of 2,4,5-triisopropylstyrene and 2,6-dimethoxystyrene have been prepared.

5. An explanation based on stereochemical grounds is given for the absence of steric hindrance in the polymerization of 2,4,5-triisopropylstyrene and 2,6-dimethoxystyrene; an explanation is also given for the occurrence of steric hindrance in the polymerization of 2,6-dimethyl-4-tertiarybutylstyrene and 2,4,6-tri-(fluoromethyl)styrene.

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THE INDIRECT VINYLATION OF MONOCARBOXYLIC AND HYDROXY ACIDS

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The synthesis of vinyl esters of organic acids and acetylene is familiar not only in the laboratory but also in industry [1]. The use of vinyl acetate for the transesterification of the corresponding acids [2] is a new application in the preparation of similar substances. We have attempted to replace the vinyl acetate by more readily accessible compounds—the vinyl ethers. It should be mentioned that the interaction of vinyl ethers and monocarboxylic acids has only been studied for incomplete acylals. This reaction proceeds when the starting components are taken in molecular proportions and heated. If an excess of vinyl butyl ether and an acid catalyst is used, then the main product obtained is a vinyl ester.

The mechanism of the formation of vinyl esters from acids and vinyl ethers is shown in the following scheme. At first an incomplete acylal (1) is formed. With excess of vinyl butyl ether the acylal is converted to an ion and then to an ester (2).

$$H_2C{=}CHOC_4H_9 + RCOOH \rightarrow CH_3CH(OC_4H_9)(OCOR) \quad (1)$$

$$CH_3CH(OC_4H_9)(OCOR) + H_2C{=}CHOC_4H_9 \rightarrow CH_2CH(OC_4H_9)(OCOR) + \text{[illegible]}$$

$$+ CH_3\overset{+}{C}HOC_4H_9 \rightarrow CH_2{=}CHOCOR + CH_3CH(OC_4H_9)_2. \quad (2)$$

In this way, evidently, conditions are created which promote the fission of the elements of butyl alcohol and the transfer of the acylal to a vinyl ester.

The vinyl butyl ether transesterification reaction brought about by monocarboxylic acid and hydroxy acids proceeds most successfully when the proportions are 1 molecule of acid to 5 molecules of ether. This process, because of its simplicity, is more suitable and accessible than the direct vinylation of acids. Experiments have shown that phosphoric anhydride is a specific catalyst; this is used together with phosphoric acid also in the direct vinylation of carboxylic acids [4]. With this catalyst the yield of vinyl esters is twice as great as that obtained with hydrochloric or sulfuric acid. The transesterification of vinyl butyl ether by means of organic acids has been most extensively studied in the case of caproic acid. The good results obtained have been extended to other acids.

From Table 1 it follows that caproic acid and vinyl butyl ether are best used in the proportion of 1:5; these give the highest yield of vinyl ester.

TABLE 1

Transesterification of Vinyl Butyl Ether by Caproic Acid in the Presence of Phosphoric Anhydride

Reaction temperature in °C	Proportion of acid and ether	Yield of vinyl ester expressed as % of acid
160-165	1:1	Traces
160-165	1:2	4
160-165	1:3	19
160-165	1:4	34
160-165	1:5	47

TABLE 2

Transesterification of Vinyl Butyl Ether by Organic Acids in the Presence of Different Catalysts.

Acid	Reaction temperature, °C	Yield of vinyl ester calculated on acid % with catalyst.		
		HCl	H_2SO_4	P_2O_5
Acetic	115-120	none	none	1
Proprionic	130-140	"	"	2
Butyric	140-150	19	20	45
Valeric	150-160	18	19	47
Caproic	160-165	17	20	47
Lactic	90-100	7	7	15
β-Hydroxybutyric	120-135	8	9	18

The transesterification of vinyl butyl ether by caproic acid proceeds with a spontaneous rise in temperature up to 160-165°. The reaction continues for one hour, including the time required for the temperature to drop to the initial. With a 5-fold excess of vinylbutyl ether over the quantity of acid taken, as well as vinyl caproate $H_2C{=}CHOC_5H_{11}$ there are formed butoxyethylidine caproate $CH_3CH(OC_4H_9)OCOC_5H_{11}$, dibutyl acetal $CH_3CH(OC_4H_9)_2$, butyl caproate $C_4H_9OCOC_5H_{11}$, and also traces of butyl alcohol C_4H_9OH and acetaldehyde CH_3CHO. When caproic acid reacts with 1-4 equivalents of ether, the same products are formed but the quantity of vinyl caproate (Table 1) is less and the yield of incomplete acylals increases. The use of 6-7 equivalents of ether in the reaction mixture does not affect the yield of vinyl caproate.

The transesterification of vinylbutyl ether by monocarboxylic acids C_2 to C_5 (Table 2) showed that this process is similar to the one described for caproic acid The rise in temperature due to the exothermic reaction effect reaches a value close to the boiling temperature of the starting acids. Under these conditions vinyl acetate and vinyl propionate were obtained in small quantities (1-2%). An attempt to increase the yield of these esters by raising the temperature to 160-170° (autoclave) gave negative results. It is also of interest to note that the formation of vinyl lactate and vinyl hydroxybutyrate takes place at a temperature considerably below the boiling point of lactic (122°/15 mm) and hydroxybutyric (130°/12 mm) acids. Of the three catalysts tried the best was found to be phosphoric anhydride.

TABLE 3

Characteristics of Vinyl Esters of Monocarboxylic Acids and Hydroxy Acids

Name and formula of ester	B.p. °C	d_4^{20}	n_D^{20}	MR_D Found / Calculated
Vinyl butyrate $C_3H_7COOCH{=}CH_2$	112-113.0	0.9121	1.4057	30.745 / 31.205
Vinyl valerianate $C_4H_9COOCH{=}CH_2$	134-136.0	0.9070	1.4102	35.025 / 35.843
Vinyl caproate $C_5H_{11}COOCH{=}CH_2$	168-170.0	0.8965	1.4160	39.824 / 40.481
Vinyl lactate $CH_3CHOHCOOCH{=}CH_2$*	151-153.0	1.0604	1.4088	27.060 / 28.092
Vinyl β-hydroxybutyrate $CH_3CHOHCH_2COOCH{=}CH_2$	170-173.0	1.0713	1.4136	31.819 / 32.730

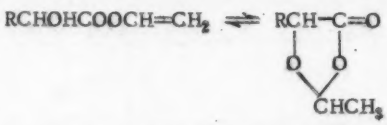
* Reported for the first time.

Note: 1) All the vinyl esters went yellow on standing.

2) The vinyl esters of the hydroxy acids were hydrolyzed by atmospheric moisture.

From Table 3 it will be seen that the boiling point of the esters increases with temperature, while the density decreases. The change in the color of the esters on storage is due to their slow oxidation by atmospheric oxygen in the presence of light. If the esters are stored in the dark or in colored bottles they undergo practically no change.

The vinyl esters of lactic and hydroxybutyric acids readily absorb moisture and hydrolyze with the separation of acetaldehyde and the corresponding acid and for this reason they must be distilled in a stream of dry nitrogen. These compounds boil within a range of 2 to 3° and their molecular refractions are lower than the calculated values. It is possible that these anomalies are due to the presence in the ethers of both a linear and a cyclic form in equilibrium.



An indirect indication of tautomery is seen in the molecular refraction values. Thus, for example, for vinyl acetate the calculated MR is 28.092, the cyclic form corresponding only to 26.359. The value found for MR is 27.060. Vinyl acetate and vinyl β-hydroxybutyrate are soluble in ethyl ether, ethanol, acetone and benzene. They are hydrolyzed to the corresponding acids and acetaldehyde, by aqueous solutions of alkalies and by mineral acids.

EXPERIMENTAL

Transesterification of vinyl butyl ester of caproic acid in the presence of phosphoric anhydride.

Starting materials: caproic acid with boiling point 202-203°; d_4^{20}, 0.9290, n_D^{20} 1.4145; vinyl butyl ether with boiling point 93.5-94°; d_4^{20} 0.7790; n_D^{20} 1.4025, and phosphoric anhydride—air dry.

Into a round-bottomed 3-necked flask are placed 23.2 g (10.2 moles) of caproic acid, 100 g(1 mole) of vinylbutyl ether and about 0.1 g of phosphoric acid; the flask is fitted with a mechanical stirrer, a mercury seal, a large capacity reflux condenser connected to a bulb trap, and a thermometer reaching to the bottom of the flask. On mixing, the temperature of the reaction mixture rose and after 15 or 20 minutes after the commencement of the experiment the temperature reached 80-85°. The flask was cooled with ice-water, the temperature rising to 160-165°. The mixture was then cooled to room temperature over 35-40 minutes. After the reaction had concluded traces of acetaldehyde (characteristic odor) were observed in the trap.

After the brown mixture had been neutralized with potash and the residue filtered off, 72.5 g (75% of amount taken) of vinylbutyl ether was distilled off at 93-98°. The vinylbutyl ether was treated with metallic sodium and had the following constants after distillation: boiling point 93.5-94.0°; n_D^{20} 1.4025. The constants of the ether separated agreed with those of that taken in the reaction. The residual mixture was distilled under reduced pressure in a stream of dry nitrogen and the following fractions were obtained:

Fraction 1 boiling point 30-40°/3 mm; 15.2 g; n_D^{20} 1.4150
Fraction 2 boiling point 42-46°/3 mm; 3.6 g; n_D^{20} 1.4083
Fraction 3 boiling point 57-63°/3 mm; 2.3 g; n_D^{20} 1.4108
Fraction 4 boiling point 85-90°/3 mm; 16.2 g; n_D^{20} 1.4128
Fraction 5 resinous residue in the flask 5.3 g; not further investigated.

Loss 6.6 g; collected in trap 1.5 g; n_D^{20} 1.4140.

Repeated distillation of fraction 1, combined with the contents of the trap under normal pressure gave a substance with the following characteristics: b.p. 168-170°; d_4^{20} 0.8995; n_D^{20} 1.4160, which corresponds to vinyl caproate. Literature data: b.p. 169-170°; n_D^{20} 1.4160 [5]. Yield 13.35 g (47%).

Hydrolysis of vinyl caproate by ethanolic potassium hydroxide
Found %: $C_5H_{11}COOCH{=}CH_2$ 98.3 and 101.52.

On hydrolysis, acetaldehyde separated as found by its characteristic odor. Vinyl caproate decolorized bromine water and added hydrogen. In the latter case it was hydrolyzed to ethyl caproate.

Hydrogenation of Vinyl Caproate

20 g of freshly distilled vinyl caproate (0.2 mole) and 5.8 g of Raney nickel catalyst (20% by weight of starting ester) were placed in a half-liter autoclave. Hydrogen was admitted and an initial pressure of 90-130 atm. was established in the autoclave. It was then rotated. After an hour the temperature had increased to 32°, and the hydrogen added vigorously. The hydrogenation was completed in 2-3 hours. After room temperature and constant pressure had been established in the autoclave, the mixture was withdrawn and distilled in a Favorsky flask under normal pressure. Double distillation gave chemically pure ethyl caproate; b.p. 151-152°; d_4^{20} 0.8649; n_D^{20} 1.4046; yield 26.0 g (89% of theory). The literature gives: b.p. 151°; d_4^{20} 0.8648; n_D^{20} 1.4045 [5].

Fraction II was treated with metallic sodium. The precipitate was filtered off and the filtrate redistilled. A pure substance (2.1 g) with b.p. 184-185°; n_D^{20} 1.4090 was obtained. The data points to its identity with dibutylacetal.

Fraction III, after redistillation had the constants; b.p. 61-62°/3mm; n_D^{20} 1.4110; d_4^{20} 0.8636. Yield 1.7 g (0.5%). These constants correspond to butyl caproate $C_5H_{11}COOC_4H_9$.

Hydrolysis of butyl caproate by ethanolic potassium hydroxide
Found %: $C_5H_{11}COOC_4H_9$ 99.12 and 98.96.

Fraction IV was redistilled in a current of dry nitrogen under reduced pressure A yield of 13.33 g (28%) of butoxyethylidene caproate was obtained; b.p. 88-90.0°/3 mm; n_D^{20} 1.4140.

Hydrolysis and determination of butyoxyethylidene caproate through the acid
Found %: $CH_3CH(OC_4H_9)OCOC_5H_{11}$ 99.4 and 101.2

Transesterification of the Vinylbutyl Ester of Lactic Acid

Starting materials: lactic acid with b.p. 122°/15 mm; d_4^{20} 1.2400; 18 g (0.2 mole); vinylbutyl ether with b.p. 93.5-94°; d_4^{20} 0.7790; n_D^{20} 1.4022; 100 g (1 mole); phosphoric anhydride —air-dry 0.1 g.

The experiment was carried out in the same way as the previous one. After the catalyst had been introduced, the maximum temperature reached by the mixture was 90-100°. The mixture darkened and resinified. After treatment with potash the filtrate was fractionated in a current of dry nitrogen; the following fractions were obtained:

Fraction 1 b.p. 92-94°; n_D^{20} 1.4020; 89.4 g
Fraction 2 b.p. 148-153°; n_D^{20} 1.4069; 5.4 g
Fraction 3 b.p. 180-184°; n_D^{20} 1.4092; 4.3 g
Fraction 4 b.p. 188-189°; n_D^{20} 1.4196; 5.6 g
Loss(by difference) 13.3 g

Fraction I, after treatment with sodium, redistilled at 93-94°; n_D^{20} 1.4022; d_4^{20} 0.7790. The constants correspond to vinylbutyl ether. Recovery from the reaction 85.1 g (85.1%).

Fraction II, after a second redistillation showed the following constants: b.p. 151-153°; d_4^{20} 1.064; n_D^{20} 1.4088; yield 3.5 g (15%); Found MR 27.060; calculated for $C_5H_8O_3$ MR_D 28.092.

Found: M 115.19; 114.31 (cryoscopic in benzene solution)
Calculated: M 116,114
Found %: C 51.66; 51.50; H 7.28; 7.08
$C_5H_8O_3$. Calculated %: C 51.72; H 6.94
Hydrolysis and determination of vinyl lactate through acetaldehyde
Found %: 98.4; 95.7
Hydrolysis and determination of vinyl lactate through the acid
Found %: 100.7; 100.1

Fraction III, after treatment with metallic sodium, had the following characteristics: b.p. 184-185°; n_D^{20} 1.4089. The constants correspond to dibutylacetal. Yield 3.4 g.

Hydrolysis and determination of dibutylacetal through acetaldehyde
Found %: 98.6; 100.6.

Fraction IV, after twice redistilling, had b.p. 188-189°; n_D^{20} 1.4195; d_4^{20} 0.9683; yield 5.2 g (13.4%). This material corresponds to butoxyethylidene lactate [6] $CH_3CH(OC_4H_9)OCOCHOHCH_3$. Found MR 48,556; calculated for $C_9H_{18}O_4$ MR 48.585.

Found: M 185.21; 193.83 (cryoscopic in benzene solution).
Calculated: M 190.234
Found %: C 57.10; 56.88; H 9.65; 9.64
$C_9H_{18}O_4$. Calculated %: C 56.84; H 9.47
Hydrolysis and determination of acylal through acetaldehyde
Found %: 96.8; 96.2

Transesterification of Vinylbutyl Ester of β-Hydroxybutyric Acid

Starting materials: β-Hydroxybutyric Acid, m.p. 49°, b.p. 130°/12 mm, 10.4 g (0.1 mole); vinylbutyl ether, b.p. 93-94°; n_D^{20} 1.4024, 50 g (0.5 mole); phosphoric anhydride 0.05 g.

The synthesis and separation of the products were carried out as in the previous experiment. The temperature of the reaction mixture rose spontaneously to 135°. Redistillation separated: 43 g (86%) of vinylbutyl ether; 2.35 g (18% as shown by the acid) of vinyl-β-hydroxybutyrate and 3.8 g of dibutylacetal. Vinyl-β-hydroxy butyrate $CH_3CHOHCH_2COOCH{=}CH_2$ had b.p. 170-173°; d_4^{20} 1.0713. n_D^{20} 1.4136; found MR 31,819; calculated for $C_6H_{10}O_3$ MR 32,750.

Found M 129.4; 124.1 (cryoscopic in benzene solution).
$C_6H_{10}O_3$. Calculated: M 130.24.
Found %: C 55.57; 55.78; H 7.69; 7.72
$C_6H_{10}O_3$. Calculated %: C 55.35; H 7.69
Hydrolysis and determination of vinyl-β-hydroxybutyrate through the acetaldehyde.
Found %: 96.8, 95.3.
Hydrolysis and determination of vinyl-β-hydroxybutyrate through the acid
Found %: 100.1; 100.6

Dibutylacetal $CH_3CH(OC_4H_9)_2$ had b.p. 185°, n_D^{20} 1.4090.

Hydrolysis and determination of dibutylacetal through acetaldehyde
Found %: 95.2; 96.2

SUMMARY

1. A new method is proposed for the indirect vinylation of monocarboxylic and hydroxyacids by transesterification of the corresponding acid with the readily available vinylbutyl ether in the presence of phosphoric anhydride.

2. The vinyl esters are obtained in 47% yield.

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THE CHLORINATION OF HYDROLYSIS LIGNIN

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Hydrolysis lignin, which is obtained in large quantities as a by-product of the hydrolysis industry, is a high-molecular-weight compound whose structural elements consist of phenols, and it is therefore a potentially valuable material which might find uses in different branches of the national economy. However, hydrolysis lignin is infusible, insoluble, chemically of low activity and it cannot be decomposed into valuable low-molecular-weight compounds by simple methods. It seemed to us that the chlorination of lignin is one of the methods by which it could be converted to a reactive state. Lignin occurring in the walls of plant cellulose and isolated from plants is easily chlorinated by treating these materials with chlorine. The properties of the chlorolignin obtained are determined by the nature of the starting materials, the chlorine content and the chlorination conditions. The chlorination is accompanied by the evolution of hydrogen chloride.

There is disagreement as to the nature of the interaction of chlorine with lignin. Some workers, studying the halogenation of lignin, consider that chlorine and bromine react with lignin only by substitution [1, 2, 3], while others consider that, as well as substitutions, additions also take place [4, 5]. When lignin is chlorinated, a loss of methoxyl groups occurs. Harris, Scherrer and Mitchell [5] found that fir lignin containing 17.3% of OCH_3 had only 6.1% after chlorination. The OCH_3 content of lignin is reduced in a somewhat lesser degree by bromination. Hibbert and his co-workers [4] also observed a reduction in the content of OCH_3 groups on halogenation. According to Harris [6], lignin sulfate from hard wood loses one-third of its methoxyl on chlorination, while for lignin of soft wood the loss is about two-fifths. Harris, Scherrer and Mitchell found that when lignin is chlorinated hydroxyl groups are lost. According to these workers, lignins when they are chlorinated both in CCl_4 and in water are neither methylated nor acetylated. Unfortunately, the halogenation conditions are not given. From these short literature references it will be seen that the chlorination of lignin proceeds in a complicated manner and is accompanied by side reactions.

In chlorinating hydrolysis lignin we avoided an excess of chlorine and high temperatures in order not to destroy the lignin molecule and we carried out chlorination under mild conditions; at low temperatures (20°) and with the required quantity of chlorine in the dark and in both carbon tetrachloride and water without a catalyst. Chlorination at a high temperature with a large excess of chlorine leads to the destruction of the side chains in the lignin molecule [7].

EXPERIMENTAL

Technical hydrolysis lignins from the Leningrad and Archangel hydrolysis factories, the characteristics of which are given in Table 1, were chlorinated:

TABLE 1

Source of lignin	Content of reducing substances in %	Content of lignin %	Resin content %	Acid content, calc'd as H_2SO_4 %
Lignin from the Leningrad factory	2.47	88.23	4.57	1.2
Lignin from the Archangel factory	2.34	93.54	9.26	1.53

Lignin ground in ball mill was extracted with boiling water, air-dried at room temperature and then twice extracted with dichloroethane to remove resins (boiling under reflux for four hours). The lignin was filtered off, washed with dichloroethane, dried in air and then over P_2O_5. 50 g samples of lignin were used for chlorination and this was carried out in dark vessels with ground stoppers, by shaking with chlorine water or chlorine solution in carbon tetrachloride for an hour at 20°.

The chlorine water was prepared by saturating water with chlorine at 12°. The chlorine in carbon tetrachloride was prepared by passing a stream of chlorine into cold carbon tetrachloride. The concentrated solution

TABLE 2

Expt. No.	Quantity of Cl_2 required (%)	Quantity of Cl_2 obtained (%)	Yield of chlorolignin, as % of initial	OH group content, (%)	OCH_3 group content (%)	Composition of substance calculated on C_9	
1	2	3	4	5	6	7	
Chlorination in CCl_4							
Lignin of the Leningrad hydrolysis factory							
Starting lignin			–	7.83	9	$C_9H_{10.06}O_{3.35}$	
1	5.0	4.77	99.12	8.37	–	–	
2	10.0	10.0	91.62	6.53	7.30	$C_9H_{8.45}Cl_{0.57}O_{4.18}$	
3	20.0	19.53	95.91	6.56	–	$C_9H_{8.01}Cl_{1.22}O_{3.91}$	
4	30.0	27.33	88.50	6.58	3.92	$C_9H_{8.34}Cl_{1.86}O_{3.69}$	
Chlorination in CCl_4							
Lignin of the Archangel hydrolysis factory							
Starting lignin			–	9.16	–	–	
1	5.0	5.00	–	8.59	–	–	
2	10.0	9.89	–	–	–	–	
3	20.0	18.39	–	8.04	–	–	
4	25.0	22.26	–	7.06	–	–	

of Cl_2 in CCl_4 was kept in dark vessels with ground stoppers, but the chlorine water was prepared directly for each experiment and analyzed. The chlorine water and the solution of Cl_2 in CCl_4 were used in quantities calculated for the substitution reaction, that is twice the quantity to be introduced into the lignin. Usually the chlorine water contained 5-6 g Cl_2 per liter and the proportion of chlorine necessary for the reaction was determined. In chlorinating with the carbon tetrachloride solution the proportion used was 1:1.5.

From the Leningrad lignin, samples of chlorolignin containing ~5, 10, 20, and 30% of chlorine were prepared by chlorination both in water and in CCl_4: from the Archangel lignin, samples were prepared containing ~5, 10, 20, and 25% of chlorine. The chlorine was quantitatively removed from the reaction solutions (no reaction with starch iodide paper). In the preparation of highly chlorinated lignins, insignificant traces of chlorine remained in the solutions. The chlorinated samples were thoroughly washed with water until the washings were neutral to methyl orange, then dried at first in air and finally in a vacuum desiccator over P_2O_5. The highly chlorinated products were colored orange-brown. All the samples were analyzed for chlorine, hydroxyl groups, and methoxyl groups.

The hydroxyl groups were determined by Verley's method. Since treatment of the chlorolignins in pyridine resulted in elimination of part of the chlorine as HCl, and since the chlorolignins contain active hydrogen groups titratable by alkali, a blank experiment was carried out in each case: the sample of chlorolignin was heated with pyridine under the Verley conditions. In calculating the percentage of hydroxyl groups, a correction was made for the number of milliliters of alkali used in the blank experiment.

Because several samples of chlorolignin, especially those highly chlorinated, dissolved in pyridine with the formation of dark solutions which were difficult to titrate with phenolphthalein, in all cases we used the titration method in which a drop of the solution was removed on a strip of filter paper previously moistened with thymol-blue indicator solution, which sharply changes at a pH close to that of phenolphthalein. The paper was dried before use. The end of the titration with alkali was determined by the formation of a pale blue streak. The blank titrations were carried out in the same way. The methoxyl groups were determined by the Kirpal-Byun method. The results obtained are shown in Table 2.

Average weight of structure link	Content of OH groups in the starting lignin calculated on the structure chain of chlorolignin	Content of OCH_3 groups in the starting lignin calculated on the structure link of the chlorinated lignin	Quantity of chlorine required (%)	Quantity of chlorine obtained (%)	Yield of chlorolignin (% of initial)	Content of OH groups (%)	Content of OCH_3 groups (%)
8	9	10	11	12	13	14	15
			Chlorination in H_2O				
			Lignin of the Leningrad hydrolysis factory				
171.7	–	–	–	–	–	7.83	9.00
–	–	–	5.0	6.15	92.09	7.28	–
204.64	6.57	7.55	10.0	12.40	95.97	6.47	4.62
222.03	6.05	6.96	20.0	19.37	100	6.00	–
241.48	5.57	6.36	30.0	24.02	95.81	–	1.38
			Chlorination in H_2O				
			Lignin of the Archangel hydrolysis factory				
–	–	–	–	–	–	9.16	–
–	–	–	5.0	7.01	–	8.13	–
–	–	–	10.0	10.52	–	–	–
–	–	–	20.0	20.03	–	8.42	–
–	–	–	25.0	20.65	–	7.26	–

From Table 2 it is evident that on chlorination in carbon tetrachloride the quantity of chlorine introduced into the lignin is close to that taken (5, 10, 20, 30% and 5, 10, 20, 25%). On chlorination with chlorine water, deviations from the amounts taken are observed. For low degrees of chlorination, the Cl content is higher than that taken (I, II) and for high degrees (IV) lower than that required. Only with 20% of chlorine is the quanitity of halogen introduced equivalent to that required. The data are the same for the lignins from the Leningrad and Archangel factories.

Evidently, when lignin is chlorinated in CCl_4 at 20° in the absence of moisture, the reaction is mainly substitution (somewhat lower contents of chlorine compared with the amounts required in the highly chlorinated preparations may be explained by the loss of chlorine when these are treated in fairly concentrated solutions in CCl_4). On chlorination with chlorine water there is a deviation from the main type of reaction.

The percentage OH group content determined with allowance for the acidity of the preparations and for the HCl eliminated is independent, apart from small variations, of the chlorine content in the samples chlorinated both in CCl_4 and in H_2O. If it is reckoned that the molecular weight of the structural elements of chlorinated lignin is higher than the starting, then the theoretically calculated quantity of OH groups in the chlorolignins should be lower than in the starting lignins. In calculating the average weight of the elementary lignin link and the average weights of the elementary links in the chlorolignin molecules, elementary analyses were used.

From columns 5 and 9 in Table 2, it is evident that the content of OH groups in lignin on chlorination closely corresponds with the calculated values, consequently the OH groups of lignin do not appear to take part in the chlorination, or the number of groups disappearing during the process is compensated for by the destruction of the lignin. This does not agree with the results of American investigators, who consider that on halogenation the hydroxyl groups of lignin disappear (it is true in the paper the method of halogentaion is not given). The content of OCH_3 groups in chlorinated lignin decreases as the chlorine increases. A marked decrease is observed when chlorination is in water. This agrees with the results already known in the literature.

SUMMARY

1. Technical hydrolysis lignin is easily chlorinated at 20° by solutions of chlorine in carbon tetrachloride or by chlorine water. When 25-27% of chlorine is introduced, the latter is quantitatively removed from the solution by the lignin.

2. The chlorine content of products chlorinated in carbon tetrachloride is very close to that required by calculation for the substitution reaction.

3. When lignin is chlorinated both in carbon tetrachloride and in water at 20° in the absence of excess chlorine and catalysts, the number of hydroxyl groups in the lignin remains unchanged. These results do not agree with those obtained by American authors who consider that hydroxyl groups are removed from lignin by halogenation.

4. The content of methoxyl groups in lignin is reduced on chlorination even under mild conditions. The reduction is especially marked when chlorination is carried out by chlorine water.

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OBITUARY

GEORGY VLADIMIROVICH AKIMOV

On January 23, 1953, after a serious illness, there passed away the outstanding physical chemist of our country, the greatest representative of Soviet science in the field of corrosion and metallurgy, Georgy Vladimirovich Akimov.

In the development of the science of corrosion of metals our country has always occupied one of the leading places. The outstanding successes in the science of metal corrosion in the past twenty years are indissolubly connected with the name of the talented Soviet scientist-Communist Honored Worker in Science and Technology, Georgy Vladimirovich Akimov.

G.V Akimov was born in 1901 in the family of a teacher at a trade institute. On finishing his secondary education in 1915, G.V. Akimov entered the Physical-Mathematical Faculty of Moscow State University. However circumstances at that time did not allow G.V. Akimov to continue his education. As a 17-year old youth he entered the ranks of the Red Army as a volunteer and took an active part in the Civil War. While he was still in the Red Army, in March 1920, Georgy Vladimirovich entered the ranks of the Communist Party and tirelessly served the cause of the Party until the last days of his life. At the end of the Civil War Georgy Vladimirovich was demobilized in order that he might continue his education at the Moscow Higher Technical Institute in the Chemical faculty, and he began to specialize in metallurgy and treatment of metals. In 1926, G.V. Akimov graduated from the Chemical Faculty of the MYTU, receiving the degree of Engineer-Technologist, and began his scientific and engineering work in the aviation industry, which at that time was not only founded. Our country was faced with the problem of mastering and creating new corrosion resistant light alloys, stainless and heat-resistant steels required for aeroplanes and other engines. Georgy Vladimirovich ardently undertook the solution of these problems.

G.V. Akimov founded the first laboratory specializing in corrosion and carried out deep theoretical and practical investigations on metal corrosion. Even the early work of G.V. Akimov was noted for its scientific depth, its originality and for its great practical importance. The following are the most important investigations which he carried out in 1927-1932: A study of the corrosion behavior of duralumin in contact with other metals; a method for the protection of aluminum alloys with the aid of protectors; the study of the corrosion behavior of riveted seams and the establishing of suitable composition of rivets; the protection of aluminum alloys with the aid of metallization, etc.

In 1927 G.V. Akimov discovered and explained the protective action of zinc on aluminum and its alloys, although in the literature of the time it was held that such a protection was not possible. In the same year, discussing results obtained on metallic contacts, G.V. Akimov arrived at the concept of multielectrode systems. In 1928, G.V. Akimov wrote the monograph "Metals and Alloys in Chemical Plant Construction", which for a long time was the only guide on the corrosion behavior of metallic materials.

In 1929-1931 G.V. Akimov carried out a series of researches on stainless steels and developed new steels. The range of his scientific researches was constantly widening.

In 1931, G.V. Akimov, for the first time, organized a Department of Metal Corrosion in the Moscow Institute of Non-Ferrous Metals and he gave the first lectures in the course.

In 1933-38 Georgy Vladimirovich undertook the wide development of the theory of multielectrode systems, the elucidation of the loss in corrosion processes with oxygen and hydrogen depolarization, the study of non-equilibrium electrode potentials of pure metals insolid solution. The results of these researches were given to a series of conferences and published, both as articles and as individual monographs.

As a result of the scientific and pedagogic activity of G.V. Akimov, a school of Soviet corrosion specialists, the largest in the world, has been founded.

In 1939, G.V. Akimov was elected a corresponding member of the Academy of Sciences, USSR. From that time, as well as carrying out his work in the aviation industry, G.V. Akimov guided the work on metal corrosion in the Institute of Physical Chemistry, Acad. Sci. USSR. An outstanding feature of the laboratories founded by G.V. Akimov was their close and indissoluble connection with industry, which permitted them to put the latest scientific advances into practice. In 1947, G.V. Akimov organized a commission on the prevention of metal corrosion under the Division of Chemical Sciences Acad. Sci. USSR and this carried out fruitful work under his

leadership and direction—the work on the prevention of metal corrosion in our country. Under his guidance a network of corrosion stations was organized in the USSR and a number of important problems was solved.

From 1949 until his death, G. V. Akimov was Director of the Institute of Physical Chemistry Acad. Sci. USSR and at the same time he continued to direct the Division of Corrosion of the same Institute as well as the VIAM Laboratories. From that time G.V. Akimov was a member of the Editorial Committee of the Journal of Physical Chemistry. The scientific activity of G.V. Akimov was many-sided. His fundamental investigations in the field of metal corrosion are well known; among them the following may be specially mentioned :

1) Work on the irreversible electrode potentials of metals of importance in the theory of corrosion. In this work the importance of non-equilibrium potentials in corrosion processes was first shown and an extremely large amount of experimental material was obtained and the theory of irreversible potential developed.

2) Work on the theory of multielectrode galvanic systems and their application to corrosion problems. The concept of corroding metals as multielectrode systems was first put forward by G.V.Amikov in 1927.

In recent years, G.V. Akimov and his students completed the development of the theory of multielectrode systems and this permitted the solution of very important theoretical and practical problems in the corrosion of complex metallic systems.

3) Work on the study of the electrochemical properties of protective films in which the connection between protective films and electrochemical factors (the existence of anode, cathode and inert areas) was first shown. In this work, it was also unambiguously shown that there was a connection between the passsivity of stainless steels and protective films.

4) Work on the mechanism of the corrosion process. G.V. Akimov and his school made an especially large contribution in the field of corrosion processes with oxygen depolarization. As is known, these processes include the most important technical cases of aluminum and iron corrosion. Here new relationships were discovered and explained; for example, the nature of the connection between the corrosion current and the cathode area: the dependence of the corrosion current over a wide range on changes in the ohmic resistance, the initial electrode potential and anode area.

5) Work on the study of microgalvanic elements in which, with the aid of refined methods of investigation on actual structure components of alloys, the quantitative confirmation of the microelement hypothesis was obtained.

6) Work on the electrochemical and corrosion behavior of metals and alloys in oxidation.

G.V. Akimov was also widely known for his work in the field of the physical chemistry of metals. He published a number of papers on the internal transformations and the technological properties of stainless steels, which played an important part in the development of stainless steel production in the USSR. He directed work in the field of physical methods for the study of metals, including the field of electron microscopy and ultrasonic defectoscopy of heat-stable alloys, steels and aluminum alloys.

The Theoretical work of G. V. Akimov enabled him to solve a number of practical problems, of which the following are the most important:

(1) the development of new methods for the protection of aluminum alloys;

(2) the development of methods for the protection of construction work;

(3) the development of methods for the prevention of gas corrosion;

(4) the development of new methods for the physical chemical study of metals.

G.V. Akimov published about 200 scientific papers. In addition to these scientific papers, he wrote 5 monographs and one textbook. Of these, his book "Theory and Methods of Investigation of Metal Corrosion" was awarded a Stalin prize. For his outstanding work in the study of the electrochemical protection of films Georgy Vladimirovich was awarded the D.I. Mendeleev prize in 1952.

For his fruitful scientific work G.V. Akimov was twice decorated by the Government with the Order of Lenin, with the Order of the Red Banner of Labor and was three times awarded the Stalin prize. He was also made an Honored Worker in Science and Technology.

The progressive Soviet Scientist-Communist, G.V.Akimov, succeeded in skillfully combining deep theoretical studies with the solution of practical problems. G.V. Akimov selflessly gave of his strength and his knowledge for the benefit of our great motherland. The memory of Georgy Vladimirovich, an outstanding patriot of our country, will always be preserved in the history of our national science.

CHRONICLE

DIVISION OF CHEMICAL SCIENCES, ACADEMY OF SCIENCES, USSR

A general meeting of the Division was held on March 27th, 1953, at which Acad. M. M. Dubinin, Division Acadamecian-Secretary, reported on the work of the Division. At the same meeting a new Bureau was elected. Members of the Division and also members of the scientific administrative staffs of chemical institutes took part in the meeting.

In his address, Acad. M. M. Dubinin said that the most important activity of the Division was the directing of the institutions which were placed under its control. This was effected by developing, in co-operation with institutes of the Division, future plans for the development of chemical science within the framework of the Academy of Sciences; by laying down the direction scientific work should take and the set-up of institutes; by combining yearly plans of institutions in the Division and approving working plans. The Division checked the fulfilment of plans for scientific work and received the yearly reports of institutes on their scientific work. The work of the Division also included the organization of research on complex scientific problems and the coordination of the activities of chemical institutions, Republican Academies of Science, and branches of the Union Academy. In the work of the Division, great attention was paid to the introduction of the results of completed scientific work into the country's national industry.

In addition, the scientific work of the Division included the organization of conferences, discussions and general meetings, the direction of the work of Division Commissions, the general direction of chemical journals published by the Academy of Sciences, and of publications of both Commissions and Institutes. The training of personnel for the Institutes and the control of personnel also came under the Division. From this it could be seen — the speaker pointed out — how wide and diverse were the functions of the Division.

Turning to the question of the organization of new institutions and the development of scientific research, Acad. Dubinin said that in recent years a number of new research institutions had been set up within the framework of the Division; these included: The Institute of Silicate Chemistry and The Institute of High-Molecular-Weight Compounds (in 1948). The structure of existing institutes had been changed, and in this reorganization a number of new laboratories had been set up.

Over a period of three years new commissions had been formed; these included: The Commission for the Development of the Scientific Heritage and Publication of the Works of A.M. Butlerov and the Commission for Chromatography. In addition, several commisions, the activities of which were valueless, were abolished.

In the Division Institutes research work on a number of new problems was taken up; these included problems on the theory of chemical structure and reactivity, on high-molecular-weight compounds, on silicate chemistry etc. Research on organo-element compounds made significant progress; work on the synthesis of heavy organic chemicals, on analytical chemistry, on corrosion, on kinetics and on adsorption was greatly extended. The most modern methods such as X-ray structural analysis, electron miscroscopy etc. were more widely used.

The Division Bureau paid great attention to the making of plans for the development of chemical sciences in the Academy organization so as to fulfil the decisions of the XIX Congress of the Communist Party of the Soviet Union. The historic task set by the XIX Congress for the further development of progressive Soviet Science so that it should occupy the first place in world science has inspired the members of the Division. The leaders concerned had shown great creative team-work in the presentation of reports on various branches of chemistry.

Turning to the question of the introduction of completed scientific work into national industry, the speaker pointed out that in recent years the bonds between the chemical institutes of the Academy and industrial undertakings and Ministerial research and planning organizations had been greatly extended and strengthened. A polular movement had developed in our country with the slogan of socialist cooperation between workers in science and industry, and its influence was felt on the work of the Academy chemical institutes.

In 1951 the total number of agreements on cooperation entered into by institutes of the division amounted to about 70, but in 1952, according to incomplete figures, it exceeded 150. Most of the agreements relate to the following institutes: IOKh (Institute of Organic Chemistry), 46; IKhS (Institute of Silicate Chemistry), 32; IONKh (Institute of General and Inorganic Chemistry), 27; IFKh (Institute of Physical Chemistry), 25.

In 1951 the chemical institutes of the Division introduced a total of 25 projects, and 23 in 1952. In 1951 the introduction of 15 projects was completed; in 1952, 8 were completed and 5 were tested with good results on the factory and pilot-plant scale, i.e., a total of 13.

Acad. Dubinin then dwelt on the nature of the more important projects introduced into industry. A number of important projects in the chemical institutes were at the introduction stage.

The speaker then remarked that in addition to the projects introduced by the institutes, there were also projects which were worked out and introduced in industry in consultation with the Academy's institutes. The work of IONKh and the Hydrochemical Institute on the investigation of soil salinity and salt deposits on canal routes and on the hydrochemical investigation of rivers and other water routes was of great importance.

However, by way of self-criticism, remarked Acad. Dubinin, — the number of projects introduced their importance in the national economy and the rate of their development were far from satisfactory, and we could not be satisfied with them. The reasons for this lay in lack of clarity of purpose and weak organization in the work of the Division, and of the Academy as a whole, in introducing completed projects. Instead of maintaining close contact with industrial organizations at the stage of laboratory investigations, when corrections and modifications could be introduced, our institutes only turn to industry when the basic work has been concluded; it frequently happens that some essential features of the process have not been fully dealt with and this leads to differences of opinion as to whether the process is ready to be introduced. Another cause of the difficulties is to be found in the lack of enthusiasm among industrial workers for the introduction of Academy of Sciences projects.

Socialist cooperation permits the union of the forces of the Academy institutes with those of industry at the earliest stages; these forces can work out the technological conditions, make an authoritative examination of the raw material, plant and economic problems and both sides can show a full development of initiative. The early cooperation of Academy institutes with industrial research and planning institutes can be especially fruitful. In this connection some Academy institutes should be strengthened by the addition of chemical technologists to the staff.

It is necessary that the forces of the institutes should be mobilized for the all-round increase in the rate of introducing new projects and for strengthening our bonds with industry; the main forces should be concentrated on the solution of large and important problems of the national economy, leaving the secondary and less important problems to factories, laboratories, and high-school departments.

Acad. Dubinin then dealt with the important field covering cooperation in scientific research between institutes of the Academy of Sciences, USSR, and Academies of the Republics. A great part in cooperation was played by visiting sessions held in conjunction with Republican Academies. Recently the Division of Chemical Sciences held four joint visiting sessions: with the Latvian SSR Academy of Sciences, with the Georgian, with the Ukrainain, and with the Uzbek SSR Academy of Sciences. It should be mentioned that each succeeding session was an improvement on the previous one. Thus, during the last joint session in Tashkent, conferences were organized dealing with all the main projects of the Division institutes. This was of no small significance for the coordination of scientific research.

The joint sessions were important events in the scientific life of the republics. As a rule they aroused great interest in the part of the governments of the republics, party organs and the chemical fraternity.

In spite of some deficiencies and irregularities, the work of coordination made definite progress; as a result there was a marked movement in the chemical institutes of the Republican Academies toward the concentration of forces and resources on the solution of fundamental tasks, appropriate to the scientific set-up of each particular institute.

The Bureau of the Division received and discussed the reports of the directors of independent chemical institutes, for example of the former Tadzhik branch, and of the Crimean and Kirgiz branches.

During the last two years the methods of coordination between the personnel of Republican Academies had been perfected. In 1951 coordination was achieved through special sessions of the Division; in 1952 (in practice at the beginning of 1953) through the Division institutes working on individual problems with confirmation of decisions by a plenum having the character of an enlarged Division Bureau.

The main deficiencies in this complex work were due to the tardy reviewing of work and examination of the plans of coordinating centers and institutes. Several reviewers gave superficial and vague decisions. The organization of cooperative work left much to be desired. In the main, coordination amounted to correcting and improving the working plans of institutes, and in particular in excluding the less important work, and in

indicating desirable directions in which chemical research might be carried out. However, big, fundamental changes in institute plans were not achieved. Therefore, the plans of the Chemical Division and those of the chemical institutes of the Republican Academies of Sciences and of the branches cannot be considered as comprising a unified plan.

A decided improvement is need in coordination to do away with awkward multiple plans, and to replace them by a single plan for the development of chemical sciences, with the Academy system as a basis for coordination.

Turning to the question of the arrangements for sessions, conferences and meetings of the Division. the speaker first remarked that the idea of general meetings of the Division was to provide an opportunity for making scientific contacts in the discussion of papers on important theoretical research of general interest. The main aim in presenting the papers was to develop discussions, because critical examination promotes the formulation of more correct ideas. Many chemists from various scientific and higher educational institutions were invited to the meetings.

In the last three years 26 session of the division were held, consisting of 50 meetings with 114 papers. Of these, 12 meetings were held in connection with the anniversaries of great events in the history of national science.

During this period, members of the Division presented 55 papers at the regular meetings; and Science Fellows at the Academy of Sciences chemical institutes, about 30 papers. Scientists from other research institutions also presented papers; these included: A.V. Kirsanov, 4 papers (Dnepropetrovsk Metallurgical Institute), K. P. Mishchenko (Leningrad Technological Institute), I. N. Plaksin (Institute of Mining, Acad. Sci. USSR); M.L. Chepelevetsky (NIUIF); A.N. Pudovik (Kazan Branch), S.V. Kaftanov, G.S. Zhdanov (Karpov Institute) A.I. Kiprianov, Ya.N. Fialkov, E. A. Shilov, V. A. Reiter (Academy of Sciences, Ukr. SSR); R. Ya. Levina, N.I. Gavrilov (Moscow State Univ.); Yu. G. Mamedaliev (Academy of Sciences, Azerbaidzh. SSR), and others; in all. 20 papers were presented.

The attendance of Division members at regular meetings was not high. In the period 1949-1952 several members did not present even a single paper at regular meetings.

Conferences and congresses on special branches of science, usually on one theme, are an important part of the Division's scientific activity. Conferences at which the full text of papers was first published were the most complete. The presentation of the paper took ten minutes and about 70% of the available time was occupied by the discussion. Here the work of the Commission on High-Molecular-Weight Compounds deserves special mention.

The Division held the following conferences and congresses:

In 1949 Conference on Gas Analysis (Commission on Analytical Chemistry); Conference on High-Molecular Weight Compounds, devoted to general questions on the chemistry and physical chemistry of high-molecular-weight compounds; Conference on the Scientific and Technical Application of Photography and Cinematography.

In 1950: Second All-Union Conference on Physico-chemical Analysis; All-Union Conference on Microelements. Conferences on: Electrochemistry, Chromatography, Chemistry of Complex Compounds, Stainless Steels, Color Photography and Cinematography, The Molecular Weight of Polymers, Electrochemical Methods of Analysis. Fourth Congress on Hydrochemistry (Novocherkask).

In 1951: The All-Union Congresses on the Theory of Chemical Structure, On Metal Corrosion in Sea Waters of the Caspian Basin (Baku), On Fundamental Problems of Scientific Photography (Odessa); The Second All-Union Congress on the History of Native Chemistry (Leningrad); Congress on Classical Methods of Chemical Analysis and Congress on the Technique of Cinematography, Sensitometry. and the Application of Cinematography to Medicine (Leningrad).

In 1952: Discussion-Conference on the Principle of the Trans-Effect and on Metal Alloys (IONKh, Acad. Sci. USSR); Conferences on the Theory of Ion Exchange. Synthesis and Application of Ion-Exchange Materials (jointly with the Commission on Vapor of High Parameters), and the Seventh Conference on the Chemistry and Physical Chemistry of High-Molecular Weight Compounds (Leningrad).

In carrying out the decisions of the All-Union Congress on the Theory of Chemical Structure (1951), two special congresses were held: In Erevan — on the relation between chemical structure and pharmacological activity; and in Kiev — on the mechanism of organic reactions. The decisions of all conferences and congresses were discussed and confirmed by the members of the Division Bureau. In 1953, it is proposed that a symposium be held on chemical kinetics. In the future. the Division Bureau must pay more attention to improving the subject-matter and the organization of conferences, making them more influential. and having the most timely topics discussed.

Turning to the activities of the Division in connection with the directing of chemical journals, Acad. Dubinin made a number of criticisms. During the past few years much work had been done in reviewing the composition of editorial committees. In particular the principle of having the same member sitting on several different editorial committees—previously a common practice—was changed. The new editorial committees were made up of scientists who could take an active part in the life of the journal, i.e., referee the papers, maintain a punctual attendance and participate in the meetings of the committee.

There were a number of deficiencies in the editorial work of chemical journals, which had not been made good even now, although they had been pointed out to the editors when their reports had been considered by the Division Bureau, and instructions had been issued. In the first place the complaint relates to the publication of discussions of the basic problems of chemistry. The publication of discussions was particularly poor in the Journal of General Chemistry, The Journal of Applied Chemistry, and The Colloid Journal. The Editors adopted a policy of laissez-faire toward the supply of papers. The Editorial Committees did not organize the presentation of papers on most important fundamental questions in different branches of chemistry. Papers published in some journals have been of poor quality scientifically.

In some journals there is a lack of esprit de corps in the work and not all members of the committee are called upon to referee papers. There is a long delay in having papers refereed. The attendance of some members is unsatisfactory.

Another deficiency in editorial work is the long delay in the publication of papers, which is sometimes as much as two years after they have been sent in. The Division constantly points out to editors that they should reduce the length of papers in editing and also make greater use of small type. However, these measures alone will not be sufficient—the portfolio of papers held by many journals still remains large, amounting to a two-years run (Journal of General Chemistry, Journal of Applied Chemistry, Journal of Analytical Chemistry); the volume of a number of journals must therefore be increased or some other radical measures taken.

The Division increased the volume of three journals since 1952; the Bull. Acad. Sci. USSR, Div. Chem. Sci. was increased by 30 printed sheets in a year (from 7 to 12 sheets per number); the journal Progress in Chemistry was doubled in size (12 instead of 6 numbers per year); the Journal of Physical Chemistry was increased by 24 sheets per year (from 8 to 10 sheets per number). In order to relieve the editorial portfolio of the Journal of General Chemistry, the Praesidium the Academy of Sciences USSR had decided to issue as a supplement to the journal, requiring separate payment, two collections of papers amounting to over 100 printed sheets.

The question of relieving the congestion in the Journal of Applied Chemistry and in the Journal of Analytical Chemistry has not yet been resolved.

The work of editors and editorial committees demanded of them more serious consideration of the essentials of their business in connection with the making of radical decisions to improve the lay-out of the journals and take measures to ensure that papers would be published not later than 6 months after receipt.

Academician Dubinin then dwelt at length on the selection, education, training and assignment of scientific personnel. He quoted numerous examples of poor work in dealing with personnel problems in several institutes.

In many institutions of the Division, self-criticism in the work of the directorate, academic councils and colloquims continued at a low level. Criticism and self-criticism had still not become fundamental methods by means of which errors and deficiencies in scientific work could be detected and overcome. One of the causes of the unsatisfactory position in the development of criticism and self-criticism in institutions of the Division, as had been justly noted at meetings of the more active members, was the passive attitude of a number of members of the academic councils of some institutes, among which should be mentioned, the Institute of Chemical Physics, The Institute of General and Inorganic Chemistry, and the Institute of Organic Chemistry.

In this connection it should be mentioned that criticism and self-criticism was not sufficiently developed in the work of the Division Bureau itself, where the lack of activity of a number of members had been observed.

Neither did the directors reports on the recent meetings on personnel contain sufficient self-criticism. Thus, for example, in the report of the director of the Institute of General and Inorganic Chemistry, Corr. Member of the Academy of Sciences, USSR, I. V. Tananaev, there were no concrete proposals for the development of criticism and self-criticism at the institute; the report of the director of the Institute of Organic Chemistry, Prof. V.V. Korshak, also showed similar deficiencies.

In all institutes the work of training personnel through post-graduate and doctorate courses was far from satisfactory, and also the training of staff personnel. Thus, for example, in 1952 the Institute of High-Molecular-

Weight Compounds did not produce one Candidate in Science from their modest number of post graduate students. During the existence of this institute, not a single Candidate's or Doctor's dissertation had been presented by its Fellows, although the demand for qualified personnel in this institute is keenly felt. It should be mentioned that the leaders and laboratory directors of this institute have not paid proper attention to initiating young workers to post-graduate work, and they have taken no measures to organize the preparation of highly qualified workers by means doctorate courses.

Such a large institute as the Institute ofPhysical Chemistry planned to have 6 post-graduate students present Candidates' dissertations in 1952. However only one student presented his dissertation within the required period; the remaining five were long delayed. Moreover, in 1952 two students left the Instituteof Physical Chemistry without presenting Candidates' dissertations, and three without presenting Doctors'.

During the whole of the existence of the Laboratory of Peroxide Compounds, not a single Candidate received his degree on the basic work of the laboratory--the synthesis of peroxides. Drs. Chem. Sci. S.Z. Makarov and V.I. Mikheeva have not given sufficient attention to post-graduate work.

Of 7 post-graduate students passing out from the Institute of General and Inorganic Chemistry in 1952, one presented his dissertation in time and the others were 1 to 9½ months late. In the past year, in this large institute, only 4 students were accepted for post-graduate work: in addition one took up post-graduate work without giving up his main work; this is entirely unsatisfactory. This institutehas a number of leading workers--Drs. Chem. Sci. M.M. Yakshin, A.M. Rubenshtein, A.D. Gelman, A.V. Babaeva, V.G. Tronev, V.I. Goremykin and others-- who pay insufficient attention to the training of scientific workers. The institutedoes not make proper use of its highly qualified personnel for the training of future Doctors of Science.

Serious deficiencies in training through post graduate work and doctorates also occur in the Instituteof Chemical Physics, where the scientific leaders pay insufficient attention to post-graduate work, which as a rule is not carried out in the time required. Several leaders (Corr. Mem. Acad. Sci. USSR V.N. Kondratyev,I.L. Zelmanov) entrust post-graduate students to other persons. Only one student presented a dissertation in the IKhF high-voltage section during the last few years.

A number of similar deficiencies in the development of personnel also occurs in the Institute of Geochemistry and Analytical Chemistry, and also in the Instituteof Silicate Chemistry.

Affairs are somewhat better in the Instituteof Organic Chemistry; however, here also only 80% of the Candidates -students presented their dissertations within the required period. Some leaders (Dr. Phys., Math., Sci., A.I. Kitaigorodsky, Dr. Chem. Sci. A.E. Borisove, Corr mem. I.N. Nazarov and others) did not present their students in time. During a long period of work at the IOKh, a Corr Mem. I.V. Obreimov and Dr. Chem. Sc. A.M. Rubenshtein did not present a single post-graduate student. The Laboratory for Intermediates and Dyes, directed by I.V. Obreimov has had no post-graduate students up to now. A number of leading Fellows (Corr. mem. I.V. Obreimov, Acad. B.A. Kazansky, Corr. mem. I.L. Knunyants and others) have not paid due attention to the preparation of students for the doctorate.

There are also material defects in the Division institutes in the training of staffs. In some institutes due attention is not given to politico-ideological work among the leading workers, especially such forms of political preparation as participation in the University of Marxism-Leninism. Thus, for example, during the entire period of existence of the Institute of High-Molecular-Weight Compounds, no Fellow with a science degree has graduated from the University of Marxism-Leninism. In the Instituteof Physical Chemistry none of the leading workers is studying the University of Marxism-Leninism courses.

Concluding this part of his report, Acad. Dubinin mentioned some concrete measures for improving the work of educating and training of scientific personnel. Acad. Dubinin closed his report with the following words:

> "May I express my confidence that the development of genuine business-like and sound criticism in the spirit of the instruction of the XIX Congress of the Communist Party of the Soviet Union will promote the improvement of the work of the Division of Chemical Sciences in all its branches."

After the report of the Academician-Secretary of the Division, Acad. Dubinin, the meeting was opened to discussion; several Academicians,Corresponding Members, and Scientific Fellows of the Division Institutes took part in the discussion.

In the discussion of Academician Dubinin's report there took part: Academicians G.G. Urazov, and P.A. Rebinder, Corresponding Members N.A. Izgaryshev, S.N. Danilov, A.D. Petrov, A.F. Kapustinsky, N.I. Nikitin, A.P. Vinogradov, I.A. Kazarnovsky, V.I. Spitsyn as well as Fellows of the institutes.

At the same meeting a new Division Bureau was elected composed of the following: Academicians N.N. Semenov and A.V. Topchiev, Corresponding Members A.P. Vinogradov, S.N. Danilov, I.L. Knunyants, V.I. Spitsyn, I.V. Tananaev, Doctors of Chemical Sciences N.I. Shuikin and K.T. Poroshin.

CONFERENCE ON CHEMISTRY OF THE BORATES

On October 23 and 24,1952, a conference on the chemistry of the borates was held in the Institute of Chemistry of the Latvian SSR Academy of Sciences in Riga. About 100 people participated in the work of the conference. The first day was devoted to theoretical, and the second to practical problems of borate chemistry.

Opening the Conference, the Director of the Institute, A.F. Ievinsh, pointed out that although boron as an element was known for about 150 years and several of its compounds were used in ancient times, the chemistry of boron compounds had been poorly studied. To-day boron was of great practical importance. Boron was in demand not only in the chemical and other industries but also in agriculture.

In the Institute of Chemistry of the Latvian SSR Academy of Sciences work on the chemistry of the borates was carried on by a small group of workers. This work had led to the synthesis of a number of new borates. Work in the same field was being carried on in other research institutesin the Soviet Union. It therefore seemed useful to hold a conference on the chemistry of boron in order to discuss the results obtained in recent work and to exchange information so that the direction of further work in this field should be marked out. Moreover, such a conference would enable personal contacts between scientists to be strengthened and this was of great value.

The first speaker, A.D. Keshan (Institute of Chemistry, Acad. Sci. LSSR) in his paper "Problems of Borate Chemistry" considered as the main problem the extension of the sources of boron compounds by utilizing natural brines and industrial effluents which contain small quantites of boron together with large quantities of other salts. For the solution of this difficult task a detailed knowledge of boron chemistry was needed. But our knowledge in this field is still meager and superficial. During the last two decades, Soviet chemists have done much in the field of borate chemistry. The boron minerals of the Indersk deposits had been studied; A.V. Nikolaev had developed the well-known field method of investigationg boron minerals; the nature of borate re-arrangement on heating had been discovered and investigated; in co-operation with A.G. Kurnakov and N.M. Selivanova a number of natural borates had been synthesized and also several artificial borates.

In the Institute of Chemistry of the Latvian SSR Academy of Sciences, work had been carried on since 1947 on the synthesis of heavy metal borates. About 20 borates had been obtained and the methods of preparing others had been improved.

Little had been done up to now on the structure of borates. Even for such a well-known and comparatively simple compound as borax, different workers had proposed four different structures. The synthetic borates of the divalent heavy metals provided valuable material for the application of methods of studying structures— electrical conductivity, cryoscopy and X-ray analysis. Whatever the method used for extracting boron—precipitation, co-precipitation, sorption or selective ion-exchange with anionites— a knowledge of the fundamentals of the process was essential for successs. Therefore, in addition to applied work it was necessary to carry on theoretical work on the chemistry of the borates.

G.K. Gode (Instituteof Chemistry, Acad. Sci. LSSR) in his paper "The Synthesis of Borates in Aqueous Solution" pointed out the importance of several factors, such as: the composition of the precipitating reagent, the proportions and concentrations of the starting materials. In the exchange reaction with equivalent quantities of borax and calcium chloride in the solid phase, calcium tetraborate was not obtained but a precipitate with a ratio of B_2O_3: $CaO = 1.6$; but in the liquid phase the ratio was 2.4. Here there is a step-wise change in the pH of the liquid phase. If the precipitating reagent is chosen with a pH corresponding to the constitution of the borate being prepared, the amorphous precipitate which separates at first crystallizes fairly rapidly. From a mixture of borax and sodium hydroxide at pH 11, the diborates of Ca, Sr and Ba crystallize out in 1-2 hours. From a mixture of borax and boric acid, the same elements give crystalline hexaborates after several days. A considerable excess of reagent is always necessary; the excess acts as a buffer in stabilizing the pH of solution. Amorphous precipitates of heavy metals, obtained by precipitation of borax solutions, are converted to crystalline higher borates after several days in boric acid, for all borates are very soluble in boric acid.

A.G. Kurnakova (Instituteof General and Inorganic Chemistry, Acad. Sci. SSR) reported on the results of studies of ternary and quaternary systems with boric acid and the oxides of calcium, magnesium, sodium, and potassium as components in aqueous solution at 25°.

The study of these systems was intended to throw light on the origin and conditions for the mutual transformation of the boron minerals in the Indersk deposits. Both natural inonite, inderite, borosodocalcite, inderborite and synthetic borates had been obtained with different ratios of B_2O_3: RO It was notable that in the systems examined, none of the slightly soluble borate compounds, the native borates, for example colemanite, askarite, hydroboracite etc., the main minerals in the Indersk deposits, were obtained. Thus, of the calcium borates, instead of the sparingly soluble pandermite $4CaO \cdot 5B_2O_3 \cdot 15H_2O$ and colemanite, $2CaO \cdot 3B_2O_3 \cdot 5H_2O$, the more soluble native borate inonite, $2CaO \cdot 3B_2O_3 \cdot 13H_2O$, was obtained. Of the magnesium borates, instead of askarite, $2MgO \cdot B_2O_3 \cdot H_2O$, the principal Indersk mineral, the more easily-soluble inderite, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$.

Most of the native borates obtained in the studies of these systems were metastable compounds. In nature under the corresponding conditions they are converted over a long period into less hydrated and less soluble stable forms— colemanite, pandermite, ascharite and hydroboracite.

Ya.Ya. Yarzhemsky (All-Union Geological Research Institute) reported on the geological structure of the Indersk borate deposits and on the nature of the raw materials available for conversion into boric acid and borax.

M.G. Valyashko (VNIIG) reported on coprecipitation of boric acid from the liquors obtained in the preparation of boric acid from boron minerals. These liquors contain 1 to 2% of boric acid. About 90% of the boric acid could be co-precipitated with magnesium hydroxide. The precipitate was, however, difficult to filter and its B_2O_3 content was low.

L.E. Berlin (NIUIF) reported on the use of manganese, calcium and magnesium to precipitate boric acid from the mother liquors obtained in the production of boric acid. He had studied the solubility of manganese borates of different compositions in water and in solutions of boric acid, borax, magnesium sulfate and sodium chloride at 25°. In water the manganese borates are hydrolyzed and the hydrolysis increases with time. The manganese borate which tended to decompose least was the one having the ratio B_2O_3: $MnO \approx 1$, obtained by precipitation from alkaline solution. The results obtained were applied on the technological scale. After manganese sulfate had been added, the solution was neutralized with calcium or magnesium oxide. After the precipitation the liquid phase contained 0.37-0.60% of B_2O_3. Studies were also carried out on the precipitation of boric acid from these solutions with the aid of small quantities of MgO. It was then found that 90% of the B_2O_3 in the initial solution passes to the precipitate. The results were tested on the production scale.

K.G. Gode (Institute of Chemistry Acad. Sci. LSSR) reported on the extraction of boric acid from dilute solutions with the aid of calcium chloride and magnesium chloride and also by ion exchange. For the precipitation with calcium chloride the best pH was 9.5; after the precipitation the liquid phase then contained 0.25% B_2O_3. The bulk of the calcium borate is precipitated in 24 hours. When calcium chloride is replaced by magnesium chloride, the precipitate settles more slowly over 28-35 days. 0.3% of B_2O_3 is retained in the liquid phase.

Only pure solutions of boric acid had been used up to now in the experiments with ionites. Types MMG, MG, TH and H had been tried. Up to 90% of the boric acid was absorbed by ionites after several days under static conditions from solutions containing .0.2% B_2O_3; the B_2O_3 content of the liquid phase falls to 0.02 - 0.03%. The ionite must be regenerated with sodium hydroxide. The action of ionites on salt solutions has not yet been tried.

Research Student V.V. Khadorchenko (Riga) reported the results of studies on the ternary system "copper hydroxide - boric acid - water" at room temperature. The reaction between copper hydroxide and boric acid is slow; after 45 minutes certain types of compund were obtained and different types after 115 days. These compounds were insoluble in water and were not decomposed by prolonged boiling, but they were easily decomposed by acids and by ammonia solution. After precipitation several hundredths of a per cent of B_2O_3 remained in solution. Perhaps this effect might be used for extracting boric acid from dilute solutions.

Opening the discussion on the papers, Acad. G.G. Urazov pointed out that the necessity of having boron compounds to meet the needs of the National Economy meant that a constant search must be made for new ways of utilizing native resources, and for this a knowledge of boron chemistry was of first importance. The chemistry of boron was being studied in the Instituteof Chemistry of the Acad. Sci. LSSR. Here the complexity of the conditions for the synthesis of borates had been shown: the important role of pH, the increase in acidity of the liquid phase in exchange reactions and other conditions When the right conditions had been found, sometimes only hours or days instead of weeks or months were required to prepar crystalline borates. The study of borate chemistry should be two-sided— from the point of view of their formation and occurrence in nature and from the point of view of their utilization. A scientific co-ordinating center should be set up to unite and direct the work of scientific institutions.

Corr Mem. Acad. Sci. USSR A. S. Grinberg pointed out that the work carried out in the Chemical Institute of the Acad. Sci. LSSR was interesting not only in relation to borates but also to other inorganic compounds, for example, the ferophosphates. It was often contended that preparative chemistry was becoming obsolete. But only the harmonious integration of different methods with due regard to technical applications and precise analysis would give the required results.

Corr. Mem. Acad. Sci. LSSR, L.K. Lepin expressed the opinion that many of the speakers had exaggerated the part played by the pH of the liquid phase in the synthesis of borates. From the papers it was clear that the liquid and solid phases were not in equilibrium. An increase in the acidity of the liquid phase leads to the formation of polyborate anions. This process should be studied in detail with the aid of potentiometric titrations, these being carried out over several days and weeks so that equilibrium could be established between the liquid and solid phases. On long contact of the solid and liquid phases during the exchange reactions of solid borates with salts of the heavy metals both phases should tend toward equilibrium, and these changes should be followed over a period.

G.B. Romov (Aktyubinsk Chem.Combine)remarked that the demand for boric acid increased from year to year, while the methods of utilizing the raw materials improved only slowly. The effluent losses were still high. There were a number of unsolved problems in the technology of production which was already on a proper basis, and where the solution systems used had been well studied. In the crystallization of boric acid it is desirable to cool the solutions to the lowest possible temperature, but then a low-quality product was sometimes obtained because of the high content of magnesium sulfate and other impurities in the solutions. The possibility of extracting boron from dilute solutions should be further studied, as this was demanded by considerations of national economy.

M.G. Valyashko - a representative of the producers - said that considerable quantities of boron were lost in effluents. Necessity compelled us to pay close attention to boron. Here, several methods for extracting small quantities of boron had been discussed. But it was desirable that we should know the economic side of these methods. It was not known if it is possible to use cobalt, nickel, zinc, and copper in the extraction of boron. The most promising of these are the magnesium compounds which are also the cheapest at present.

L.E. Berlin acknowledged the successes in synthesizing new borates, but this work, in his opinion, did not lead in the proper direction. Borates were obtained with expensive cations: nickel, cobalt, lead, copper. It was not known if they could be used because of this. Problems of practical importance should be developed. The report on the copper borates was interesting, but it was impossible to wait 45 or 115 days for their precipitation; ways of shortening the time should be found. Besides this process could be used only where cheap copper residues were available. In selecting a collector two factors should be taken into account; insolubility of the compounds and the economic effect. Magnesium was the most economical. Collaborative work should be carried out on the study, precipitation and extraction of boron from the precipitates obtained.

K.M. Saldadze (All-Union Reagent Research Institute) remarked that much interesting material on the chemistry of boron had been heard at this conference. The representatives of the Institute of Chemistry of the Acad. Sci. LSSR had shown that they correctly interpreted the instructions of the XIX Party Congress, "To develop technical problems on a scientific basis". A defect was the little attention paid to the economics of borate production. From other papers it was clear that great attention had been given to the working of minerals and the utilization of works liquors and natural waters, but nothing had been said about the technical production of boric acid and its salts of reagent purity, issued in large quantities for analytical and other purposes. The technique of determining small quantities of boron present as an impurity in various compounds had also not been dealt with... Precipitation of boron from solution was a more promising method of extraction than the method using ion-exchange resins. All the resins reacting with boric acid, which had been tried up to the present also adsorbed anions of other acids. Selective anion exchange resins should be obtained and also solid amines. The All-Union Reagent Research Institute was carrying out work in this direction. Insoluble amines had already been synthesized which absorb silicic, carbonic and other weak acids. These amines could probably be applied to the extraction of boron from borate waters.

RESOLUTION

As a result of the papers read and the lively exchange of views which followed, the conference reports:

1. The Conference organized by the Institute of Chemistry of the Acad. Sci. LSSR consists in a meeting of the representatives of many institutions engaged in problems of borate chemistry and the utilization of borates to satisfy the needs of the national economy.

2. As a result of the work done in the country's research institutes, a number of systems of B_2O_3 have been studied, studies have been carried out on the synthesis of a number of new borates, on methods of precipitation, on co-precipitation and adsorption of boric acid; new technical processes for the treatment of borate raw materials have been worked out; several geochemical problems have been studied.

3. This work, which gave results of practical and theoretical value, was carried out without sufficient co-ordination. In view of this, it is the opinion of the Conference that a co-ordinating center should be organized under the Praesidium of the Academy of Sciences, USSR

4. The Conference is of opinion that further work on the chemistry and utilization of the borates should take the following direction

a) Studies on borate chemistry should be extended, special attention being devoted to the structure of the borates and their composition in aqueous solution; and also to the study of technically important systems containing B_2O_3, and the elucidation of the underlying phenomenon of precipitation and adsorption.

b) Work on the geochemistry of boron in salt strata and on natural solutions should be considerably developed.

c) In the field of the technology of boron the conference considers the main tasks to be: the development of methods of treating low-grade raw materials and natural waters; the perfecting of existing methods of extraction and the study of new methods of extraction with ion exchange resins. The making of special ion-exchange resins for boron is regarded as promising.

5. In view of the importance of the work on boron, the Conference considers that an essential condition for the success of the work is the provision of a staff of Fellows together with the necessary space and equipment.

6. The Conference considers that its proceedings should be published.

7. It is hoped that another conference will be held in 1954.

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